

MODELING GEOCHEMICAL PROCESSES IN ENHANCED GEOTHERMAL SYSTEMS WITH CO₂ AS HEAT TRANSFER FLUID

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ABSTRACT

The concept whereby heat is recovered from a geothermal reservoir by replacing the native aqueous phase with essentially pure high-pressure carbon dioxide as the working fluid is referred to as an Enhanced Geothermal System with CO₂ (EGSCO₂). The concept has yet to be tested in the field, and the chemical consequences, both within the reservoir itself, and at its periphery, are not fully understood. Modeling the chemical evolution of EGSCO₂ systems over a range of operating parameters, spatial dimensions, host rock compositions and geohydrologic properties is needed, but requires substantial development beyond the current state of the art. At issue is how and to what extent this development might be required in order to answer questions that could critically affect the feasibility and successful implementation of the technology.

We review the literature on natural analogues, including wall rock alteration in gold deposits and gas-rich geothermal systems, as well as experimental studies, thermodynamic models for secondary minerals, equation-of-state formulations in the system NaCl-CO₂-H₂O and state-of-the-art electrolyte models, to gain insight into CO₂-induced fluid-rock interactions for temperatures in the range 10 - 350°C, pressures from 0.1 - 60 MPa, and salinities from 0 - 6 molal NaCl. We then propose a multi-step process through which developments in economic geology, igneous and metamorphic petrology, geothermal chemistry and the physical chemistry of electrolytes might be progressively integrated by taking advantage of existing computer codes, while simultaneously resolving critical uncertainties affecting the implementation of EGSCO₂.

INTRODUCTION

The use of supercritical CO₂ (scCO₂) instead of water

as heat extraction fluid for geothermal energy sources was suggested by Brown (2000) as a “game changing” alternative that could avoid the problems of aqueous fluids, make heretofore inaccessible energy resources available for human use, and provide ancillary benefits by using and storing CO₂. Theoretical studies have indicated that CO₂ may extract heat from fractured rock at approximately 50 % higher rates than water, with the advantage of CO₂ increasing for lower reservoir temperature (Pruess, 2006). The theoretical predictions require testing and refinement through laboratory experiments. Operating an Enhanced Geothermal System with CO₂ (EGSCO₂) would necessitate a novel step of “reservoir development” that would follow the stimulation phase, and would involve continuous CO₂ injection to displace, dissolve, and eventually remove the resident aqueous phase, thereby transforming the core of the EGS system into a reservoir of dry, essentially anhydrous CO₂. The reservoir development phase would be characterized by a complex interplay of multiphase flow processes (CO₂ displacing brine), interphase mass transfer effects (CO₂ dissolving in the aqueous phase, water dissolving into supercritical CO₂), and geochemical interactions (aqueous and anhydrous CO₂ in different parts of the system interacting with resident mineral assemblages) (Pruess, 2007). These processes operate over a broad range of space and time scales, and constitutive relationships.

The future promise of EGSCO₂ can be evaluated by considering the theoretical and practical issues of fluid dynamics, heat transfer, and rock-fluid chemical and mechanical interactions of such systems through laboratory, theoretical, modeling, and field studies. Modeling approaches must be developed, and experimentally validated, that can cope with the full range of thermodynamic conditions in an EGSCO₂, from injection of “cold” scCO₂ to production of water-CO₂ mixtures, to circulation of pure CO₂ at

“hot” reservoir conditions.

GEOCHEMICAL MODELING OF EGSCO2

Defining the EGSCO2 Environment

The broad geochemical requirement is to model chemical interactions between aqueous-phase CO₂ mixtures, reservoir rocks, and well construction materials, for the entire range of fluid mixtures, rock types and thermodynamic conditions anticipated in an EGSCO₂, including conditions with no aqueous phase present. Quantitative geochemical models simulating such interactions, coupled with hydrodynamic processes must be developed to replicate the complex multi-phase multi-component system non-equilibrium system. The modeling will be performed with a view to analyzing issues of CO₂ containment and the fate through transport and chemical reactions of CO₂ fluid losses, and identifying favorable as well as unfavorable geologic environments for EGSCO₂. The ultimate goal of such geochemical model development is to help define objectives and procedures for an eventual field test.

The range of fluid conditions expected in an EGSCO₂ are assumed to cover temperatures from ambient (injection) to reservoir conditions ($10^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$), pressures from ambient to 50 MPa or more ($0.1 \text{ MPa} \leq P \leq 50 \text{ MPa}$); fluid compositions ranging from low salinity brine up to the limits of brine saturation through brine-CO₂ mixtures to essentially dry scCO₂. The host rock types would cover a wide range of chemical compositions.

We assume that the host rock throughout the EGSCO₂ is homogeneous and coarsely fractured, i.e., hydraulically conductive fractures are present in a rectilinear grid with fracture spacings between 5 and 50 m. Within each block, the rock is fragmented by discontinuous fractures with an array of fracture widths varying between 10^{-6} and 10^{-3} m. Within the rock itself, both continuous (transmissive) and closed end (non-transmissive) pores are present with apertures ranging from 10^{-9} – 10^{-6} m. The nature and distribution of hydraulically conducting and discontinuous fractures, and the distribution of pore sizes will depend on the rock type.

A schematic diagram to illustrate a geothermal resource undergoing heat extraction using scCO₂ is illustrated in Figure 1. It is expected to comprise three distinct zones:

1. A hot inner zone or "core" of the system, from which all fracture water has been removed through displacement or

evaporation into the circulating scCO₂. The fluid consists of a single super-critical CO₂ phase with residual steam. The cores of the matrix blocks could contain residual saturated regions containing brine, which are undergoing progressive evaporation, and are held in position by capillary forces. This is the main volume from which thermal energy is extracted by the circulating CO₂.

2. An intermediate region surrounding the inner zone that contains a two-phase mixture of CO₂ and aqueous fluid, and where the scCO₂ is displacing the aqueous phase along fractures.
3. An outer region containing a single aqueous phase into which CO₂ is dissolving.

The geothermal system illustrated in Figure 1 would be representative of a typical water dominated system from which the water had been displaced by scCO₂. The temperature distribution is localized due to the proximity of an isolated heat source. Zones 2 and 3, therefore, are shown with significantly lower temperature than the core. It is conceivable, however, that a large, aerially extensive region of hot rocks might be discovered, and that temperature drop-off towards the periphery is not as marked as illustrated. Little is known about the geochemistry of aqueous-depleted systems at elevated temperatures, and the absence of mobile water in the inner zone poses unique questions, which will have to be addressed through laboratory experiments and modeling (Regnault et al., 2005; Jacquemet, 2006).

Characterizing Alteration in an EGSCO2

The secondary alteration of host rocks in an EGSCO₂ involves competition between hydrothermal alteration and carbonation reactions, where the former process facilitates the latter. Just understanding the complex interplay of processes, let alone attempting to quantitatively model their thermodynamic and kinetic aspects over the specified range of temperature, pressures and system chemical compositions presents a formidable challenge in reactive chemical transport modeling. These processes have natural analogues, primarily in mesothermal gold deposits, where the ore-forming fluids are relatively dilute (< 5 wt.% NaCl equivalent) brines containing up to 0.3 mole fraction dissolved CO₂. Geothermal fluids of similar composition, and within the lower range of pressures and temperatures observed in mesothermal gold deposits, have actually been tapped in deep wells at the Monte Amiata geothermal field in Italy (Giulio et al. 2007).

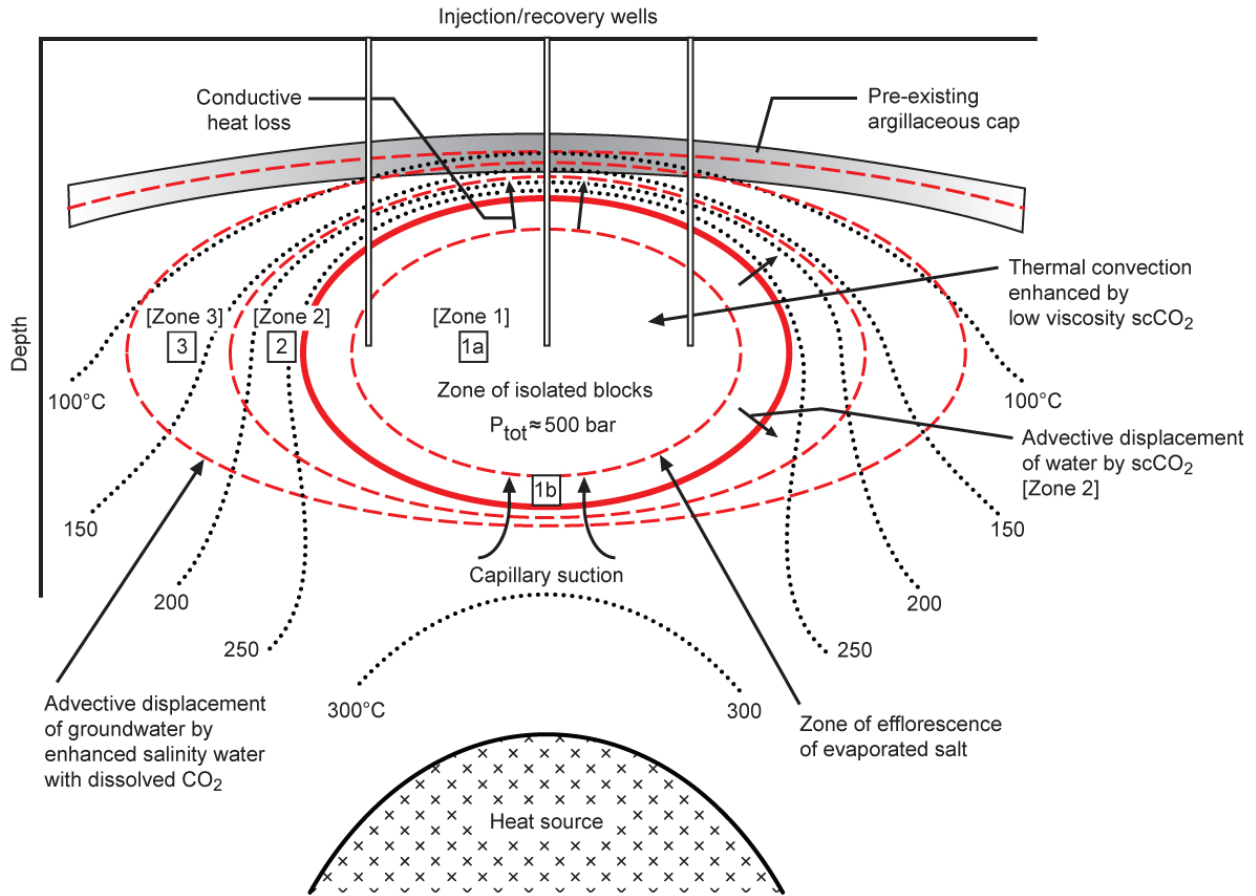


Figure 1. A schematic diagram to illustrate the geochemical zonation of a geothermal reservoir undergoing heat extraction using $scCO_2$. Discrete environments represented by 1a, 1b, 2 and 3, are discussed in greater detail in the text.

Associated wallrock alteration, involving CO_2 metasomatism, and the formation of secondary carbonates, provides much insight into what might be expected in an EGSCO₂ hosted by similar rock types. Mueller and Groves (1991) have reviewed the literature of Western Australian gold deposits and classified them into five types on the basis of their ambient P, T conditions and alteration. This classification can generally be extended worldwide to other gold deposits of similar provenance. Descriptions of mesothermal gold deposits, which formed at temperatures between 200 and 350°C are particularly pertinent.

Wallrock alteration in mesothermal gold deposits provides a qualitative basis for understanding the nature and sequence of alteration involving concurrent hydrogen and carbonate metasomatism. Furthermore, these deposits are also hosted in a diverse array of rock types, corresponding closely with those of geothermal reservoirs, but they formed over a much wider upside range of temperatures, pressures and CO_2 partial pressures than

contemplated for an EGSCO₂. This limitation can be offset by taking into account diagenetic alteration associated with petroleum maturation, which corresponds to conditions anticipated to occur in the margins of the EGSCO₂, i.e., $PCO_2 \leq 5$ MPa, T ranging between 75 and 150°C. (Coudrain-Ribstein et al., 1998). The two natural analogues therefore bracket, and in some cases overlap the P-T range encompassed by EGSCO₂.

Russian scientists contributed significantly to a theoretical understanding of metasomatic processes including those typically observed in vein-type gold deposits, especially under the scientific leadership of Korzhinskii, e.g. see Korzhinskii (1970). Russian scientists have conducted experimental studies of metasomatic processes, which have been summarized by Zharikov and Zaraisky (2003). Although conducted at temperatures and pressures somewhat higher than those of interest, it provides valuable quantitative information of the kinetics of diffusion-controlled metasomatism including that involving carbonation. An example of particular interest in

which carbonate metasomatism between 250 and 360°C was experimentally induced in a column of

comminuted quartz diorite is illustrated in Figure 2.

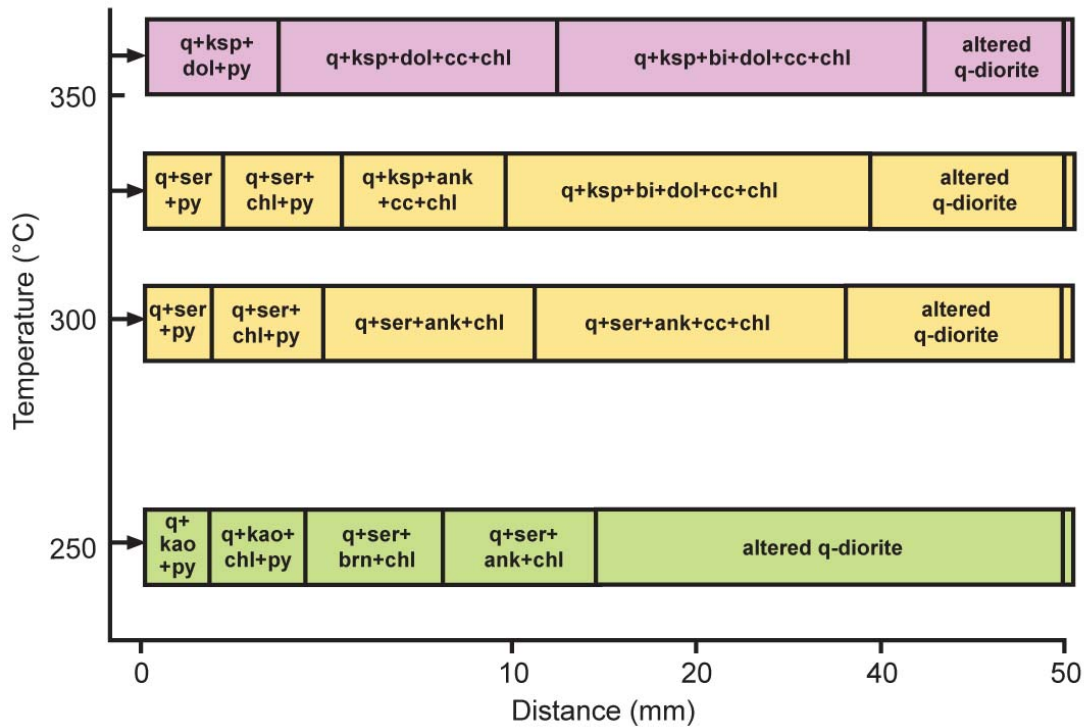


Figure 2. Experimental formation of carbonate metasomatic zones in a column of comminuted quartz diorite as a function of temperature. $P_{H_2O + CO_2} = 100 \text{ MPa}$, $X_{CO_2} = 0.1$, $\log (mKCl/mHCl) = 3.0$, $mKCl = 1.0$, total $S = 10^{-2} - 2 \cdot 10^{-2} \text{ M}$, excess quartz, $t = 336 \text{ hr}$. Scale of first 10 mm doubled for clarity. (After Zharikov and Zارايسكي, 2003)

Zharikov and Zارايسكي (2003) showed that the laboratory experiments are consistent with theory where each metasomatic replacement front generated during diffusive transport will propagate in a uniform a manner, with neither the creation, nor the elimination of intervening zones. Using experimental results cited by Zharikov and Zارايسكي (2003), the thickness of alteration zones in an EGSCO₂ after given time spans and temperatures can be calculated. For example, at a temperature of 200°C, the thickness of the hydrothermal alteration zone would approach 4 cm after 30 years exposure to a hydrothermal solution diffusing into a typical igneous or metamorphic rock.

Implicit in these calculations is the assumption that the surface rates of reaction are fast in relation to the diffusive aqueous phase transport, i.e., reaction rates are transport, rather than surface rate controlled. This is certainly true at temperatures above 300°C, and leads to the formation of sharp metasomatic fronts. However, surface reaction rates for many minerals slow greatly with falling temperature, diminishing by many orders of magnitude between 500 and 25°C, the consequence being that below $\approx 300^\circ\text{C}$, a transition

takes place between transport and surface rate control, leading progressively to a “smearing out” of reaction fronts with falling temperature.

MODELING REQUIREMENTS

Despite the obvious insights gained from natural analogues, they do not entirely replicate the chemical or physical conditions associated with an ESGCO₂. Furthermore, both the theory, code implementation, and the thermodynamic and kinetic data over the range of P, T conditions required for simulations and independent validation using natural analogues are incomplete and in some cases, rudimentary. Some of the hurdles faced in developing suitable geochemical models are detailed in the following paragraphs.

Mineral Dissolution and Precipitation Kinetics

With the transition from transport (aqueous diffusion) control to surface rate control below 300°C, the kinetics of carbonation and hydration reactions of wallrocks becomes important. Some aspects of heterogeneous reaction kinetics involving the destruction or precipitation of rock-forming minerals

have been neglected in past modeling studies of geothermal systems. One concerns the significant discrepancy between the kinetics of mineral dissolution obtained in laboratory experimental studies when compared field observations. Theoretical work over the last decade has largely accounted for this discrepancy, which relates to mineral dissolution and precipitation mechanisms. Recent work has shown that several dissolution mechanisms are operative, ranging from generalized corrosion under conditions far from equilibrium, through multiple- and single-site nucleation on crystal faces, to stepwise dissolution of single layers as equilibrium is approached. Each mechanism possesses its own distinctive kinetic rate constant, the stepwise dissolution rate constant being orders of magnitude lower than that for generalized corrosion. Another issue concerns the precipitation of metastable minerals instead under high levels of supersaturation, which usually involves the nucleation and precipitation of successively more stable forms in accordance with the Ostwald Rule of Stages. The precipitation, especially of secondary disordered hydroxy-aluminum- or magnesium-silicates retards mineral transformations at near-earth surface temperatures. Accurate modeling of rock-water reactions in an ESGCO₂ will require recognition of these phenomena.

Solid Solution Models of Multi-Component Minerals

Field observations of wallrock alteration in mesothermal gold deposits and experimental studies of metasomatism indicate that many of the hydrated secondary silicates are complex solid solutions, e.g., chlorite, biotite and white micas, smectitic clays, and at higher temperatures, amphiboles. Recent advances in metamorphic petrology have led to the development of complex solid solution models for these minerals. The thermodynamic properties of secondary carbonates, most of which fall within the system CaCO₃-MgCO₃-FeCO₃, have also been studied extensively with the formulation of appropriate regular solution models. These models, together with extensive thermodynamic databases of other rock-forming minerals, form a sound basis for modeling the thermodynamic relations between minerals in multi-component metasomatic assemblages of interest.

Electrolyte Models of the Aqueous Phase Containing Dissolved CO₂

With progressive desiccation of the country rock within an EGSCO₂ reservoir during operation, the residual aqueous phase would eventually saturate with respect to alkali metal halides and carbonates. An electrolyte model is required that can

accommodate a wide range of ionic strengths from dilute to the limits of saturation of very soluble salts in an EGSCO₂ between 100-350°C and up to 50 MPa. For validation using natural analogues, the electrolyte model must be applicable to 400°C and 400 MPa, which is beyond the limits of any current electrolyte model.

A model originally conceived to calculate the activities of non-electrolyte and dissolved gas solutes in water, the so-called universal quasi-chemical equation, or UNIQUAC equation (Abrams and Prausnitz, 1975) has recently been combined with the Debye Huckel equation for very dilute electrolytes together with extensions to describe intermediate range electrolyte interactions to model aqueous salt and miscible non-electrolytes from infinite dilution to salt saturation or even anhydrous molten salt compositions. These extended UNIQUAC equations require fewer empirical parameters than the Pitzer interaction model (Pitzer, 1973), and they are applicable over a greater range of solution compositions, and with little loss of accuracy. At least two versions of the extended UNIQUAC equation are currently in use. The first was developed primarily by Thomsen (1997). The second has been developed by the scientific staff of OLI Systems Inc., and is referred to as a mixed solvent electrolyte (MSE) model. (OLI Systems Inc., 2011). The Thomsen version has been used to model geothermal fluids to 300°C and 100 MPa, but only for sulfate and carbonate scaling minerals (Villafila Garcia, 2005). OLI Systems claims that their version is applicable over a range of T and P from -50 to 300°C and 150 MPa respectively. Although it is applicable over a wider range of salt compositions, it, too, would require further development for EGSCO₂ environments.

Other Issues

The second issue relates to the likelihood that within the scCO₂ bubble characterized by Zone 1 of the EGSCO₂ reservoir, residual brines saturating the rock matrix would become isolated domains. The isolated domains would be under capillary tension, its magnitude being directly dependent on the aqueous/scCO₂ interfacial tension, which is in turn dependent on temperature, brine composition, effective pore diameter, relative humidity, and ambient scCO₂ partial pressure. Recent investigations of capillary pressure and its effect on thermochemical equilibria in unsaturated soils at earth surface temperatures have demonstrated that negative pressures as high as ≈ 150 MPa are possible, and that such negative pressures can modify significantly the phase relations between minerals compared with what would be expected at 1 bar.

The determination of interfacial tensions and effective capillary pressures under EGSCO2 conditions presents a unique challenge. Bachu and Bennion (2009) have investigated the aqueous phase interfacial surface tension in CO₂-brine systems up to 125°C, 27 MPa P(CO₂) and 334 g/L dissolved salts. They found that the interfacial tension increases with salinity due to the salting out of dissolved CO₂ and increases with temperature. OLI Systems staff in unpublished work addressing interfacial tensions of strong mixed solvent electrolyte solutions have developed a promising approach for predicting the interfacial tension of multi-component aqueous systems that incorporates in part their MSE model, and is applicable over comparable ranges of P, T and composition (OLI Systems, 2009). Further development of the subject is required. It should also be noted in passing, that lithostatic and hydrostatic pressures in an EGSCO2 will most likely differ, and that this condition could further modify both the thermodynamics and the kinetics of the system.

THE PATH FORWARD

The foregoing discussion shows that modeling EGSCO2 geochemistry and attempting a partial validation using natural analogues will be a significant challenge. Given the zonation of an EGSCO2, it would be prudent to simulate the chemistry within representative volumes of each zone before attempting a complete integration. But before this can be accomplished, suitable geochemical models must be created.

The first requirement is to evaluate chemical equilibria in the rock-water-scCO₂ system, where the rock compositions can vary from mafic to acid. For validation purposes, equilibria should be calculated over a range of temperatures and pressures, i.e., 75-400°C and 50-400 MPa, which includes upper and lower bound natural analogues. Because both the secondary aluminum- and magnesium-silicate minerals and secondary carbonates formed during alteration are for the most part complex multi-component solid solutions, Theriak Domino (De Capitani, 2011) and Perple_X (Connolly, 2011) are particularly valuable tools for exploring such mineral-fluid phase equilibria. Initial modeling should be performed using codes that can accommodate such complexity. In addition, although the number of phases present within discrete metasomatic zones is invariant, the number of chemical potentials that are mobile determines, by Gibbs phase rule, the actual number. In an EGSCO2, the number of mobile components is likely to differ from that controlling wallrock alteration in mesothermal gold deposits. Furthermore, in

EGSCO2 scCO₂ is always present in some parts of the system, whereas in mesothermal systems, scCO₂ phase separation is not ubiquitous, and its impact on wallrock alteration is unquantifiable.

Transport, surface rate controlled and mixed regimes would be present in an EGSCO2. Sophisticated reaction schemes characterizing the precipitation or dissolution of minerals may be needed, especially below 100°C, where the formation of metastable phases may dominate the alteration scheme. Because such modeling requirements are exceptionally demanding, it may be preferable to run test cases initially to determine whether simplifications might be made without losing the required predictive accuracy. This would be especially important when considering nucleation and crystal growth, where both the mechanisms and the needed kinetic and thermodynamic parameters are incompletely known.

The extended UNIQUAC equation has obvious advantages when modeling the aqueous phase. The choice of either Thomsen or OLI Systems Inc. versions depends largely on factors independent of EGSCO2 requirements. A substantial effort will be required to develop the interaction parameter database needed to model the system over the specified range of temperatures and pressures. Once fully developed and tested, it could be coupled with phase equilibrium codes such as Theriak Domino or Perple_X to calculate the aqueous phase composition in thermodynamic equilibrium with multi-component solid-solution phases assemblages of carbonates and aluminum and magnesium-ferrous silicates at elevated temperatures and pressures as a second step.

Modeling the geochemistry of Zone 1 requires consideration of the impact of capillary pressure on both chemical equilibria and reaction kinetics in residual aqueous phase saturating regions in the country rock. A model to estimate the aqueous phase/scCO₂ interfacial tension at P(CO₂) ≤ 50 MPa and T ≤ 350°C will be required. That proposed by OLI Systems Inc. to predict interfacial tension of mixed solvent electrolytes appears to be suitable. However, extrapolation beyond the range of extant experimental data will be required. With estimated interfacial tensions for aqueous phase compositions up to the limits of saturation with respect to the contained dissolved salts, the range of capillary pressures can be estimated for given rock porosities, and the impact of negative pressures on chemical equilibria and kinetics evaluated. Only if the preliminary results indicate that capillarity effects are larger than the overall uncertainties of the model, should the effects of negative pressure be modeled fully.

Once the foregoing preliminaries have been accomplished, it would be time to put everything together and attempt to model the separate zones within and EGSCO₂. Only after suitable isothermal simulations of these zones have been tested and compared with field observations, would it be appropriate to progress to the final step of attempting a global non-isothermal simulation of a complete EGSCO₂. Several reactive chemical transport codes are available that might be modified to accomplish this task.

In looking forward, we recognize that the magnitude of the required effort is significantly greater than prior initiatives in geochemical modeling. Rapid progress would be achieved only through collaborative effort and significant expenditure of resources. However, the task, although scientifically and technically challenging, could lead to substantial rewards, not only in the development of geothermal energy, but also in enhancing our scientific understanding of geochemical processes relating to metasomatic processes, wallrock alteration and ore deposition.

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