



Guide to Recent Publications on Inorganic Water-Rock Interactions Relevant to Deep- Well Wastewater Disposal in Carbonate-Evaporite Formations in the Athabasca Oil Sands Area, Alberta



Alberta Energy and Utilities Board
Alberta Geological Survey

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1 Introduction

The rapid expansion of in situ bitumen-recovery projects based on steam-assisted gravity drainage (SAGD) technology in the EUB-designated Athabasca Oil Sands Area of northeast Alberta (e.g. Butler, 2001), has generated substantial new industry interest in the subject of waste-water disposal by deep-well injection. These projects produce a variety of liquid-waste streams requiring disposal, including steam-boiler blowdown water and excess produced water. Deep-well disposal can be an acceptable waste-management option for in situ projects, depending on site-specific circumstances. Deep-well injection of oilfield waters in the Province of Alberta is administered by the Alberta Energy and Utilities Board (EUB) as documented in EUB Guide 51 – Injection and Disposal Wells: Well Classifications, Completion, Logging, and Testing Requirements. Deep-well disposal of oilfield and industrial waste-waters in Alberta is considered to be a safe and viable disposal option where wells are properly constructed, operated, and monitored. EUB Guide 65 describes the application requirements for disposal/injection wells.

The scope of this literature review is not meant to imply or suggest that disposal-well operators or their agents have an onus to explore any or all of the issues raised in this literature review as they might relate to their particular project. Rather, this review is being put into the public domain for information only, without comment or direction pertinent to regulatory or administrative activities of the EUB or any other government agency in the Province of Alberta.

Under EUB Guide 51, matters of fluid-fluid, fluid-equipment, and fluid-formation compatibility are left primarily to the disposal-well operator. Fluid-fluid and fluid-formation compatibility in the Athabasca Oil-Sands Area are potentially of more interest to operators than in some parts of the Alberta Basin because of:

- the relatively shallow depth of disposal zones in northeastern Alberta in general;
- the degree of vertical and horizontal variability in formation-water chemistry due to cross-formational flow of formation waters;
- the more limited number of overlying and laterally confining layers isolating disposal zones from surface, relative to deeper parts of the Alberta Basin;
- the presence of structural complexities in deep strata presumably related to Paleozoic salt collapse and karsting plus differential compaction of Lower Cretaceous sedimentary rock;
- the outcropping of some potential disposal zones along the deeply incised river valleys that cross-cut the modern landscape in the Athabasca Oil Sands Area.

Because of these complicating factors, operators in the Athabasca Oil Sands Area are exercising additional due-care and attention in the design of their deep-well disposal projects. This extra care and attention often includes updating disposal designs to reflect current scientific knowledge. However, the scientific literature related to deep-well disposal has grown exponentially during the last decade, particularly with regard to issues of fluid-formation compatibility. Operators could find the sheer number of noteworthy scientific publications to be an obstacle to exercising extra due-care and attention in the permitting of their disposal projects in Athabasca. In light of this situation, the Alberta Geological Survey commissioned this review to assist the oil sands industry in accessing the relevant scientific literature in an efficient and timely manner.

The substance of this review purposely reached to the very limits of modern research into rock-water interactions in the disposal-well context. A particular emphasis was placed on publications discussing fluid-formation interaction in carbonate-evaporite sequences. This was because such rocks form the deepest and most isolated disposal zones in much of Athabasca Oil Sands Area. But for the same reasons of time and efficiency cited above, this review did not explore the scientific literature related to karsting, waste disposal in salt-caverns, nuclear waste disposal, or carbon-dioxide sequestration in geological

media. However, all of these fields have continue to produce new insights into fluid-rock interaction that may be pertinent to deep-well disposal in the Athabasca area. The hydraulics of well injection or flow of injected liquids away from a disposal well were not reviewed for the same reasons.

This review has benefited from the comments of Dr. E.H. Perkins of the Alberta Research Council.

2 Scope of Work

This report is a guide to selected publications in the scientific literature on inorganic water-rock chemical interactions that might affect the disposal of oilfield wastewater in deep carbonate-evaporite formations. Searches were restricted to literature published since the Alberta Research Council evaluation of waste-water disposal in the Cold Lake Area. (Bachu et al., 1989). The intent is to identify research that provides new data and/or models for interpreting and predicting long-term water-rock interactions in carbonate-evaporite aquifers.

In addition to papers on waste-water injection, recent contributions in petroleum engineering, groundwater geochemistry and studies of diagenesis were examined for expositions of relevant chemical processes, quantitative models and computational methods. The behaviour of complex reacting systems is often non-linear; hence theoretical work on non-linear systems was also examined. The primary literature on determination of specific thermodynamic and kinetic data is voluminous and requires careful evaluation, hence such work was not reviewed in detail. Most of this primary work is cited and evaluated in the textbooks and papers mentioned below.

3 Applicability of this Review to the Athabasca Oil Sands Area, Alberta

The utility of the cited research in the prediction of long-term water-rock interactions in the Athabasca Oil Sands Area, depends on aquifer mineralogy, formation-water composition, waste-water composition, rate of injection, regional geology and hydrogeology. There are numerous sources of these data in the public domain. Alberta-specific aquifer-mineralogy data can be found in numerous scientific papers and graduate theses or can be generated directly from core examination. The Alberta Energy and Utilities Board (EUB) maintains and curates an extensive collection of core at its Core Research Centre in Calgary, Alberta. Analyses of formation waters are similarly available from the EUB or from various private companies who provide the same data in a digital or value-added form. Waste-water compositions and rates of injection are project specific, but some of this information can be garnered from project application reports and Environmental Impact Assessments in the public record, available through the EUB and/or Alberta Environment. Completion details of injection wells are of public record and available through the EUB.

4 Textbooks

A number of advanced textbooks on water-rock interaction have been published in the last decade. These contain the essential theoretical background for understanding the papers cited below and for computing predictive models in water-rock systems. They are listed below for quick reference.

- Phillips (1991): Flow and Reactions in Permeable Rocks.
- Anderson and Crerar (1993): Thermodynamics in Geochemistry. The Equilibrium Model.
- Nordstrom and Munoz (1994): Geochemical Thermodynamics (Second Edition).
- Ortoleva (1994): Geochemical Self-Organization.
- Bethke (1996): Geochemical Reaction Modeling.
- Lichtner et al. (1996): Reactive Transport in Porous Media.
- Boudreau (1996): Diagenetic Models and Their Implementation.
- Giles (1997): Diagenesis: A Quantitative Perspective.

- Lasaga (1998): Kinetic Theory in the Earth Sciences.

In addition, Lake et al. (2002) recently published *Geochemistry and Fluid Flow*. However, this book was not available to the authors at the time of this review.

5 Wastewater Injection - Case Studies and Reviews

Bachu et al. (1989) examined the regional and local effects of deep waste-water injection in the Cold Lake area of Alberta. They reviewed the data requirements, outlined potential mineral dissolution and precipitation reactions, and performed a series of calculations to evaluate the geochemical effects of waste injection. For the formation mineralogy and water compositions available to them, they determined that the most important geochemical phenomena to be expected were the dissolution/precipitation of calcite and quartz. Their geochemical analysis was combined with calculations of rock strength and numerical simulations to provide order-of-magnitude estimates of the effects of injection. They also used mass-balance calculations to estimate the impact of precipitation/dissolution on disposal aquifers.

While the Bachu et al. (1989) study is based on equilibrium thermodynamic analysis, papers by Gunter et al. (1997, 2000) emphasize long-term kinetic effects to evaluate the aquifer disposal of acid gases. These papers contain critical evaluations of published kinetic models and rate constants. Important conclusions are that carbonate minerals will probably reach equilibrium with injected water within 10 to 40 years and that reactions of carbonates with H_2SO_4 and H_2S can cause build up of CO_2 pressure with the possibility of fracturing the aquifer. Kopperson et al. (1998) also discusses acid-gas injection with water.

An important case study by Rosenbauer et al. (1997) gives the results from experiments and computed equilibrium behaviour of brine when injected into carbonate rocks. The solubility of anhydrite decreases with increasing temperature. This was shown to be sufficient to cause precipitation of large amounts of anhydrite at the proposed injection site. The comparison of output of computer codes SOLMINEQ and PHRQPITZ with experimental results illustrates the care that must be taken when interpreting the results of predictive calculations.

Spongberg's (1994) thesis on the feasibility of deep-well injection for brine disposal includes a review of relevant chemical processes described in the petroleum engineering literature but does not provide quantitative models.

Crother and Totten (1995) have published an abstract on the geochemical consequences of deep disposal of toxic waste, but their detailed results have not yet appeared in journals.

Apps and Tsang (1996) compiled a series of papers on deep-well injection of wastes. They include groups of papers on waste interactions as well as other aspects of deep-well injection practice and engineering.

At the time of this review, The U.S. National Groundwater Protection Council maintained a website at www.gwpc.org which contained an injection-well bibliography plus links to other related sites.

6 Petroleum Engineering Studies

There is a large, established petroleum-engineering literature on the chemical aspects of water injection. These studies provide data and models for short time-scale water-rock processes and are supported by direct observation and experimental results. Many of the studies are focused on the evaluation of a particular polymer, an inhibitor, or an acidization treatment and lack detailed petrographic study or geochemical modeling. Nevertheless, they can be good sources of insight and should not be overlooked. Examples of such papers outside of the realm of direct study of injection or disposal include Coulter and Jennings (1997) and Li et al. (1998).

Older references generally provide qualitative descriptions of phenomena. Important processes are:

- Mineral precipitation (scaling) due to mixing of injected and aquifer water and/or temperature and pressure changes;
- Enhancement of permeability due to mineral dissolution;
- Mechanical destruction of permeability due to migration of fines released by mineral dissolution or clay-mineral disaggregation;
- Destruction of permeability due to clay-mineral swelling.

More recent workers have developed quantitative models of the same phenomena. Various groups have obtained a large body of experimental data to calibrate such models. The experimental studies are not referenced here, but are cited in the following selected papers, which present new equilibrium and kinetic models and derived model parameters.

Bertero et al. (1988) show the applicability of equilibrium calculations to prediction of scale formation using the EQ3/6 geochemical program.

Granbakken et al. (1991) describe a kinetic model for scale formation and provide rate constants for precipitation and dissolution of common scale minerals.

Paige and Murray (1994) discuss general experience of produced-water injection projects in oilfields.

Chang and Civan (1997) provide an empirical model for chemically induced formation damage resulting from fines migration, clay swelling and chemical dissolution and precipitation. Using the published model equations and a finite difference code, they derive precipitation rate constants, solid deposition and entrainment coefficients, cation-exchange coefficients and pore-throat plugging coefficients by fitting computed model output with laboratory core plug tests.

Atkinson and Mecik (1997) discuss the thermodynamics and effects of temperature, pressure and non-ideal solutions on the solubility of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4), barite (BaSO_4), celestine (SrSO_4) and calcite (CaCO_3). They derive heat capacity constants for the solid phases, volume changes for the solubility reactions and Pitzer coefficients for the activities of the ionic species.

Raines and Dewers (1997a) examine models of gypsum and calcite precipitation and dissolution when both surface reaction rates and hydrodynamic conditions influence kinetics.

Araque-Martinez and Lake (1999) describe a new approach to modeling equilibrium and kinetics of precipitation/dissolution reactions and their effect on well impairment.

Civan (2000) presents improved models for the interpretation and prediction of porosity and permeability in rocks in which the pore topology is evolving by geochemical and geomechanical water-rock interactions.

Also of interest is the paper by Thomas et al. (1995), which describes the use of an expert system along with the standard geochemical codes PHREEQE, PHRQPITZ and SOLMINEQ to predict potential formation damage due to chemical and mechanical processes resulting from water injection. Details of the data and algorithms used are not provided.

Bunney et al. (1996) have published an abstract on the assessment of chemical disequilibrium in oil reservoirs and implications for diagenetic modeling, but these results have not yet appeared in journals.

7 Groundwater Studies

Although the temperatures and pressures are lower than would be found in deep wells, geochemical studies of groundwater systems can provide estimates of slow reaction rates of natural processes. These studies are supported by direct observation of water chemistry and interpretations based on the output of established computer codes.

An important process recognized in these studies in carbonate rock is dedolomitization. One mechanism involves dissolution of anhydrite or gypsum, enriching the brine in Ca ions to the point of calcite saturation. As calcite precipitates, the required CO₂ is generated by dissolution of dolomite. The net result is a large increase in pore volume. This process is one of several invoked to explain the formation of karst terrains with obvious implications for water injection in anhydrite and dolomite bearing formations.

The classic study by Plummer et al. (1990) describes the results of a modeling study to determine geochemical reactions controlling groundwater chemistry in a well-studied limestone aquifer. In addition to dedolomitization, halite dissolution and sulfate reduction are found to be important. Estimates of rates of dissolution and precipitation are obtained. In a deep aquifer, dissolution processes could affect aquifer integrity, while the sulfate reduction could lead to the generation of H₂S.

Raines and Dewers (1997b) give the results of experimental and in situ dissolution of gypsum. These results and computer simulations suggest that reactive solutions can penetrate much further into gypsum-karst conduits than previously thought possible.

Ayora et al. (1998) discuss a reactive transport model of dedolomitization in which the main processes are calcite precipitation and dolomite dissolution in brines arbitrarily enriched in Ca and SO₄. Their model gives estimates of reaction rates and explains observed mineral textures.

Hill (1995) uses data on sulfur isotopes to postulate a complex series of processes for karst formation. Initially, hydrocarbons react with sulfate ions from evaporite minerals to produce H₂S. After migration, the H₂S reacts with oxygenated water to produce sulfuric acid. This in turn dissolves carbonates to form major caverns.

Other important processes recognized in groundwater systems are carbonate dissolution or precipitation resulting from mixing of different waters, even when the original waters are in equilibrium with the mineral phase. This phenomenon is due to the non-linear relationship between activities and concentrations of ionic species in natural waters. This means that two waters, initially in equilibrium with a particular mineral, may become either undersaturated or oversaturated when they mix. Giles (1997, Chapter 7) summarizes and reviews work on this phenomenon.

8 Diagenesis Studies

Diagenesis is the geological term for the processes that change sediment to consolidated sedimentary rock after burial. Diagenetic studies are based on detailed study of rock mineralogy, fabric, cementation, porosity, and formation-water chemistry. Though diagenesis generally takes place on geological time-scales, study of diagenetic processes offers much insight to fluid-formation compatibility in deep-well disposal projects.

Giles' (1997) text is a comprehensive review of quantitative methods of analyzing diagenetic processes. Of particular relevance to waste-water injection are the examples of use of modern hydrochemical studies, illustration of the use of simple mass balance models, explanations of equilibrium thermodynamic modeling, chemical kinetic modeling, fluid flow and reactive-transport computations. It has an extensive reference list of papers published up until 1994.

The review papers by James and Choquette (1990), Choquette and James (1990), Hiatt and Kyser (2000) and Hutcheon (2000) on diagenesis of limestones list a number of burial diagenetic processes in carbonate rocks. They include:

- Dolomitization of limestone;
- Cementation of limestone by carbonate and/or sulfate cements;
- Replacement of dolomite by calcite, or "dedolomitization";
- Reduction of sulfate (anhydrite) by thermal processes at temperatures greater than 140° C.

This can result in precipitation of metal sulfides and/or production of H₂S. Additional diagenetic processes are the generation of CO₂ from clay-carbonate reactions and biogenic sulfate reduction to produce H₂S.

Dolomitization can enhance or reduce permeability, depending on the process leading to dolomitization. Sibley et al. (1994) review previous work and discuss the kinetics of the reaction in experiments and natural settings. They obtain interesting conclusions on the mechanism of dolomitization and provide a compilation of rate constants. In a major paper, Arvidson and Mackenzie (1999) review the literature and present the results of a series of experiments on the kinetics of dolomite precipitation. Their work confirms a strong temperature dependence for the precipitation reaction and a moderate dependency on saturation index.

Huang and Longo (1994) conclude that silicate-carbonate reactions can be an important inorganic source of CO₂ and lead to secondary porosity. They claim the reactions are sufficiently suppressed in closed systems that they cannot contribute to overpressure formation or generate enough pressure to cause fractures. On the other hand, Desrocher and Hutcheon (1998) conclude

"that the majority of reaction mechanisms are capable, perhaps in combination with other mechanisms, of generating overpressure in the presence of realistic combinations and amounts of clay and carbonate minerals".

Simpson (1999) studied fluid chemistry in the Devonian Leduc and Nisku Formations in southern Alberta. This study contains a thorough review of processes generating H₂S: maturation of organic compounds, bacterial sulfate reduction (BSR) and thermal sulfate reduction (TSR). Only the latter two are thought to produce significant quantities of H₂S. Bacterial sulfate reduction in the subsurface appears to operate only up to temperatures of 40-50 °C, while thermal sulfate reduction is effective at higher temperatures. The kinetics of BSR reactions are reviewed in Eden et al. (1994), while Simpson's thesis summarizes the experimental and theoretical work on TSR.

9 Computer Codes for Path Modeling

Computer codes offer the means to simulate and experiment with fluid-fluid and fluid-formation compatibility issues. These codes include equilibrium as well as kinetic modeling, and offer the sophisticated user insight into rates of reaction as well as reaction-pathway analysis. Reaction-pathway analysis is important because there may be a multitude of possible reactions that a fluid-fluid or fluid-formation system can experience. Reaction-path models can identify the most likely pathways based on the physical chemistry and thermodynamic properties of the system under study. The most sophisticated codes link reaction to flow processes. As in any computer simulation, the quality of the output is proportional to the quality of the input parameters and the skill of the user.

Perkins et al. (1997) and Mäder et al. (1998) have recently published reviews of various computer codes for modeling water-rock interactions. Development of such codes and associated databases is an active

area of research. To be useful in waste-water injection calculations, such codes must be capable of handling reactions in concentrated brines at high temperatures and pressures.

Programs that use kinetic models are essential for the prediction of the long-term behaviour of subsurface brines. Three of the most popular and commercially available packages are:

- EQ3NR/EQ6 (Wolery, 1992a, 1992b, Wolery and Daveler, 1992, Daveler and Wolery, 1992) are a package of codes for solving speciation-solubility and reaction-path problems. Rate laws for irreversible reactions may be either relative rates or actual rates.
- The Geochemist's Workbench (Bethke, 2000) solves many of the same problems as EQ3NR/EQ6 and uses the same activity models and databases. It has a "user-friendly" interface and graphic output.
- GAMSPATH (Talman et al., 2000) (currently in a beta version) is similar to the code used by Gunter et al. (2000) to evaluate aquifer disposal of acid gases.

Reactive transport codes add spatial coordinates to the pathway models. Although they are not commercially available, two of the codes widely used in the academic community are OS3D/GIMRT (Steeffel and Yabusaki, 1996) and MPATH (Lichtner, 1992):

- OS3D/GIMRT is a package containing two codes that use different numerical schemes to simulate multi-component reactive transfer. All mineral precipitation and dissolution reactions are governed by a kinetic formulation. The thermodynamic database is based on EQ3/6. No hydrodynamic flow calculation is done, so the user must supply a velocity field.
- MPATH models a space-time continuum with multi-component chemical reactions using several different forms of kinetic rate laws. As with OS3D/GIMRT, the user must supply a velocity field.

Several research groups are actively developing simulators that include both hydrodynamic modeling and reactive transport capabilities. Such capability is necessary to model density driven plumes and convection cells. Liu and Ortoleva (1996a, 1996b) describe CIRF.A, a fully coupled multiphase flow, contaminant transport and fluid and mineral reaction model. The code can simulate "chemical reactions involving rock, wastes and formation fluids and their effects on contaminant transport, rock permeability and porosity and the integrity of the reservoir confining units". They have used the code to make 10,000-year predictions of the fate of waste fluids in a carbonate reservoir.

Le Gallo et al. (1997) have developed DIAPHORE to simulate water-rock interactions at a reservoir scale and times up to a few million years. The code includes the effect of chemical reaction on mineral surface areas and permeabilities.

10 Nonlinear Phenomena and Instabilities

Models of energy and mass transfer in multi-component, multi-phase systems are almost always nonlinear. Nonlinear phenomena are of particular, albeit still academic, interest in formation-fluid compatibility in deep-well disposal because they can result in local changes to porosity and permeability. Local changes can lead to fingering or self-focused flow in parts of the aquifer away from the well bore, thereby altering the dynamics of the physical and chemical system in unpredictable ways.

Studies of nonlinear phenomena in the literature concentrate mostly on the expression of nonlinear behaviour in the governing equations of physical and chemical systems. A number of mathematical phenomena that occur in the solutions of such equations have counterparts in the real world systems. The interaction of numerical error, mathematical instabilities and genuine nonlinear phenomena are difficult to disentangle in realistic mathematical models of natural systems. Nonetheless, it is important to be aware

of these phenomena when interpreting predictive calculations. All the model developers who work on reaction-path modeling (discussed above) and reactive chemical transport codes are aware of these issues.

Density inhomogeneities due to thermal or chemical processes are known to cause instabilities in flow patterns, resulting in plumes and/or convection cells (Chapter 5, Phillips, 1991). Phillips outlines mathematical methods for testing the possibility of such phenomena.

For many years, chemical engineers have been aware of the non-uniqueness of solutions of the chemical equilibrium problem, as well as instabilities and multiple solutions for the equations describing chemical reactors (e.g. Denbigh and Turner, 1984). These phenomena are also known in actual engineering practice, hence such studies are part of ongoing chemical engineering research (e.g. Bildea et al., 2001). Some reactor designs (packed bed, tubular, etc.) are described by similar equations to those used in geochemical modeling. To the extent that geochemical models can be formulated as a set of nonlinear equations, they should be tested for uniqueness and stability of solutions.

Bethke (1992) discusses the nonlinearity of the equations describing the equilibrium distribution of species in aqueous systems and the possible existence of multiple solutions to such problems. He states that most modeling software will find only a single root, so it is imperative that the modeler pays careful attention to the construction and verification of computed solutions.

In addition to multiple solutions to equilibrium or steady-state problems, nonlinearity may result in a number of phenomena in dynamic systems (Nicolis, 1995; Epstein and Pojman, 1998). These include the well-known unpredictability of chaotic systems, as well as the spontaneous appearance of various temporal and spatial patterns (self-organization). The implications of such behaviour for waste-water injection are that predictive models may not behave predictably and that self-organizing patterns may result in unforeseen spatial inhomogeneity of the water-rock system, possibly leading to the spatial localization of dissolution/precipitation reactions.

Ortoleva's (1994) monograph reviews the mathematics of pattern formation due to the nonlinear behaviour of geochemical systems. His analysis of flow-driven reaction fronts involving precipitation and/or dissolution shows how multiple fronts, trapping fronts, and reverse fronts can be generated. Dissipative structures can develop at these fronts, resulting in compositional waves and oscillations, fingering, "worm-holes" and self-focusing flows. Other phenomena he considers include unstable coarsening fronts and precipitate patterning. Of particular interest is his analysis of basin-scale reaction-driven advection phenomena (Ortoleva's Chapter 14). The direct applicability of these models to waste-injection problems is difficult to assess. Most of the models serve to provide explanations of observed phenomena rather than predict future behaviour of natural systems.

11 References

- Anderson, G.M. and Crerar, D.A.(1993): *Thermodynamics in Geochemistry - The Equilibrium Model*; Oxford University Press, Oxford, 588 p.
- Apps, J.A., and C.-F. Tsang, eds. (1996): *Deep Injection Disposal of Hazardous and Industrial Waste, Scientific and Engineering Aspects*; Academic Press, New York, 775 p.
- Araque-Martinez, A. and Lake, L.W. (1999): A simplified approach to geochemical modeling and its effect on well impairment; Society of Petroleum Engineers 56678; presented at the 1999 SPE Annual Technical Conference and Exhibition in Houston, Texas, 3-6 October 1999.
- Arvidson, R.S. and Mackenzie, F.T. (1999): The dolomite problem: the control of precipitation kinetics by temperature and saturation state; *American Journal of Science* 299, p. 257-288.
- Atkinson, G. and Mecik, M. (1997): The chemistry of scale prediction; *Journal of Petroleum Science & Engineering* 17, p. 113-121.
- Ayora, C. Taberner, C., Saaltink, M.W. and Carrera, J. (1998): The genesis of dedolomites: a discussion based on reactive transport modeling; *Journal of Hydrology* 209, p. 346-365.
- Bachu, S., Perkins, E.H., Hitchon, B., Lytviak, A.T., and Underschultz, J.R. (1989): Evaluation of effects of deep waste injection in the Cold Lake area, Alberta; Alberta Research Council Bulletin No. 60, 57 p.
- Bertero, L., Chierici, G.L., Gottardi, G., Messini, E., and Mormino, G. (1988): Chemical equilibrium models: their use in simulating the injection of incompatible waters; *SPE Reservoir Engineering*, February 1988, p. 288-294.
- Bethke, C.M.(1992): The question of uniqueness in geochemical modeling; *Geochimica et Cosmochimica Acta* 56, p. 4315-4320.
- Bethke, C.M. (1996): *Geochemical Reaction Modeling*; Oxford University Press. Oxford, 397 p.
- Bethke C.M. (2000): *The Geochemist's Workbench, A User's Guide to Rxn, Act2, Tact, React, and Gtplot*.
- Bildea, C.S., Dimian, A.C. and Ledema, P.D. (2001): Multiplicity and stability approach to the design of heat-integrated multibed plug flow reactor; *Computers & Chemical Engineering* 25, p. 41-48.
- Boudreau, B.P. (1996): *Diagenetic models and their implementation; Modelling Transport and Reactions in Aquatic Sediments*; Springer, New York, 414 p.
- Bunney, J.R., Sorbie, K.S., and Jordan, M.M.(1996): Assessment of chemical disequilibria in oil reservoirs: implications for production- and diagenetic-time scale geochemical modelling; *Annual Meeting Abstracts - American Association of Petroleum Geologists and Society of Economic Paleontologists and Mineralogists* 5, p. 20.
- Butler, R. (2001): Some recent developments in SAGD; *Journal of Canadian Petroleum Technology* 40, p. 18-22.
- Chang, F.F., and Civan, F. (1997): Practical model for chemically induced formation damage; *Journal of Petroleum Science & Engineering* 17, p. 123-137.
- Choquette, P.W., and James, N.P. (1990): Limestones - The burial diagenetic environment; *in* McIlreath, A.A. and Morrow, D.W. (editors) *Diagenesis*; Geoscience Canada Reprint Series 4; Geological Association of Canada, St. John's, p. 75-112.
- Civan, F. (2000): Predictability of porosity and permeability alterations by geochemical and geomechanical rock and fluid interactions; Society of Petroleum Engineers 58746; presented at the

- 2000 SPE International Symposium on Formation Damage Control in Lafayette, Louisiana, February 2000, p. 23-24.
- Coulter, G.R., and Jennings Jr., A.R. (1997): A contemporary approach to matrix acidizing; SPE Paper 38594.
- Crother R.A., and Totten, M.W. (1995): Geochemical consequences of deep-well injection of hazardous wastes; Annual Meeting Abstracts - American Association of Petroleum Geologists and Society of Economic Paleontologists and Mineralogists 4, p. 19.
- Daveler, S.A. and Wolery, T.J., 1992. EQPT, A data file preprocessor for the EQ3/6 software package, User's guide and related documentation (Version 7.0) UCRL-MA-110662 Part II; Lawrence Livermore National Laboratory.
- Denbigh, K.C., and Turner, J.C.R. (1984): Chemical reactor theory. An Introduction; Cambridge University Press, Cambridge. 253 p.
- Desrocher, S., and Hutcheon, I. (1998): Clay-carbonate mineral reactions; a means of overpressure generation in clastic rocks?; Geological Society of America, 1998 Annual Meeting Abstracts with Programs 30, p. 312-313.
- Eden, R.D., Laycock, P.J., and Wilson, G. (1994): Oilfield reservoir souring - model building and pitfalls; *in* Ogden, P.H. (editor) Recent Advances in Oilfield Chemistry; Royal Society of Chemistry, Cambridge. 331 p.
- Epstein, I.R., and Pojman, J.A. (1998): An Introduction to Nonlinear Chemical Dynamics: Oscillations, Waves, Patterns, and Chaos; Oxford University Press, Oxford, 480 p.
- Giles, M.R. (1997): Diagenesis: A Quantitative Perspective. Implications for Basin Modelling and Rock Property Prediction; Kluwer Academic Publishers, Dordrecht. 526 p.
- Granbakken, D., Haarberg, T., Rollheim, M., Østvold, T., Read, P. and Schmidt, T. (1991): Scale formation in reservoir and production equipment during oil recovery III. A kinetic model for the precipitation/dissolution reactions; *Acta Chemica Scandinavica* 45, p. 892-901.
- Gunter, W.D., Perkins, E.H. and Hutcheon, I. (2000): Aquifer disposal of acid gases: modelling of water-rock reactions for trapping of acid wastes; *Applied Geochemistry* 15, p. 1085-1095.
- Gunter, W.D., Wiwchar, B., and Perkins, E.H. (1997): Aquifer disposal of CO₂-rich greenhouse gases: extension of the time scale of experiment for CO₂-sequestering reactions by geochemical modelling; *Mineralogy and Petrology* 59, p. 121-140.
- Hiatt, E.E., and Kyser, K. (2000): Chapter 4. Links between depositional and diagenetic processes in basin analysis, porosity and permeability evolution in sedimentary rocks; *in* Kyser, K. (editor) Fluids and Basin Evolution; Mineralogical Association of Canada Short Course 28, Calgary 2000; Mineralogical Association of Canada, Ottawa, p. 63-92.
- Hill, C. (1995): Sulfur redox reactions: Hydrocarbons, native sulfur, Mississippi Valley-type deposits, and sulfuric acid karst in the Delaware Basin, New Mexico and Texas; *Environmental Geology* 25, p. 16-23.
- Huang, W.L. and Longo, J.M. (1994): Experimental studies of silicate-carbonate reactions I. Application to diagenesis; *Applied Geochemistry*, 9, p. 502-522.
- Hutcheon, I. (2000): Chapter 5. Principles of diagenesis and what drives mineral change; *in* Kyser, K. (editor) Fluids and Basin Evolution; Mineralogical Association of Canada Short Course 28, Calgary 2000; Mineralogical Association of Canada, Ottawa, p. 93-114.

- James, N.P. and Choquette, P.W. (1990): Limestones - The meteoric diagenetic environment; *in* McIlreath, A.A. and Morrow, D.W. (editors) *Diagenesis*; Geoscience Canada Reprint Series 4; Geological Association of Canada, St. Johns, p. 35-74.
- Kopperson, D., Horne, S., Kohn, G., Romansky, D., Chan, C., and Duckworth, G. (1998): Injecting acid gas with water creates new disposal option; *Oil and Gas Journal*, August 3, 1998, p. 33.
- Lake, L.W., Bryant, S.L., and Araque-Martinez, A.N. (2002): *Fluid flow and geochemistry; Developments in Geochemistry 7*; Elsevier, New York, 244 p.
- Lasaga, A.C. (1998): *Kinetic Theory in the Earth Sciences*; Princeton University Press. Princeton. 811 p.
- Le Gallo, Y., Bildstein, O., and Brosse, E. (1997): Integrating permeability trends in reservoir characterization using diagenesis modeling; Society of Petroleum Engineers 38004; presented at the 1997 SPE Reservoir Simulation Symposium in Dallas, Texas, 8-11 June 1997.
- Li, Y.-H., Fambrough, J.D. and Montgomery, C.T. (1998): Mathematical modeling of secondary precipitation from sandstone acidizing; *SPE Journal* 3, 303 p.
- Lichtner, P.C. (1992): Time-space continuum description of fluid-rock interaction in permeable media; *Journal of Geophysical Research* 28, p. 3135-3155.
- Lichtner, P.C., Steefel, C.I. and Oelkers, E.H. (1996): Reactive transport in porous media; *Reviews in Mineralogy* 34; Mineralogical Society of America, Washington, 438 p.
- Liu, X. and Ortoleva, P. (1996a): A coupled reaction and transport model for assessing the injection, migration and fate of waste fluids; Society of Petroleum Engineers 36640; presented at the 1996 SPE Annual Technical Conference and Exhibition in Denver, Colorado, 6-9 October 1996.
- Liu, X. and Ortoleva, P. (1996b): A general-purpose, geochemical reservoir simulator; Society of Petroleum Engineers 36700; presented at the 1996 SPE Annual Technical Conference and Exhibition in Denver, Colorado, 6-9 October 1996.
- Mäder, U., Waber, N., and Büker, C. (1998): Geochemical modeling of natural and contaminated groundwaters and diagenetic processes; Short Course Notes, 88th Annual Meeting of the Geologische Vereinigung e.V. University of Berne February 25, 1998; Geologisches Institut und Mineralogisch-Petrographisches Institut, Universität Bern. Berne, Switzerland. 127 p.
- Nicolis, G. (1995): *Introduction to Nonlinear Science*; Cambridge University Press, Cambridge. 254 p.
- Nordstrom, D.K. and Munoz, J.L. (1994): *Geochemical Thermodynamics*; Second Edition; Blackwell Scientific Publications, Oxford, 493 p.
- Ortoleva, P.J. (1994): *Geochemical Self-Organization*; Oxford University Press, Oxford. 411 p.
- Paige, R.W., and Murray, L.R. (1994): Re-injection of produced water – field experience and current understanding; *EuroRock 94*, 731 p.
- Perkins, E.H., Gunter, W.D., Nesbitt, H.W. and St-Arnaud, L.C. (1997): Critical review of classes of geochemical computer models adaptable for prediction of acidic drainage from mine waste rock.; Fourth International Conference on Acid Rock Drainage, Proceedings p. 587-601.
- Phillips, O.M. (1991): *Flow and Reactions in Permeable Rocks*; Cambridge University Press, Cambridge, 285 p.
- Plummer, L.N., Busby, J.F., Lee, R.W., and Hanshaw, B.B. (1990): Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming and South Dakota; *Water Resources Research* 26, p. 1981-2014.

- Raines, M., and Dewers, T. (1997a) "Mixed" kinetics control of fluid-rock interaction in reservoir production scenarios; *Petroleum Science & Engineering* 17, p. 139-155.
- Raines, M.A. and Dewers, T.A. (1997b): Mixed transport/reaction control of gypsum dissolution kinetics in aqueous solutions and initiation of gypsum karst; *Chemical Geology* 140, p. 29-48.
- Rosenbauer, R.J. Bischoff, J.L. Kharaka, Y.K. (1992): Geochemical effects of deep-well injection of the Paradox Valley brine into Paleozoic carbonate rocks, Colorado, U.S.A.; *Applied Geochemistry* 7, p. 273-286.
- Sibley, D.F., Nordeng, S.H., and Borkowski, M.L., (1994): Dolomitization kinetics in bombs and natural settings; *Journal Sedimentary Research* A64, p. 630-637.
- Simpson, G. P. (1999): Sulfate reduction and fluid chemistry of the Devonian Leduc and Nisku formations in south-central Alberta; Unpublished PhD thesis; Department of Geology and Geophysics, University of Calgary, 227 p.
- Spongberg, Martin Edward (1994): The feasibility of deep well injection for brine disposal; Unpublished M.Sc. Thesis; Department of Civil Engineering, Texas A&M. 120 p.
- Steeffel, C. I. and Yabusaki, S. B. (1996): OS3D/GIMRT Software for modeling multi-component-multidimensional reactive transport; Pacific Northwest National Laboratory, Richland, Washington.
- Talman, S.J., Perkins, E.H. and Gunter, W.D. (2000): Users manual for GAMSPATH (β version), A reaction path -mass transfer program; Draft.
- Thomas, L.G., Albertson, M., Perdeger, A., Knoke, H.H.K., Horstmann, B.W. and Schenk, D. (1995): Chemical characterization of fluids and their modelling with respect to their damage potential in injection or production processes using an expert system; Society of Petroleum Engineers 28981; presented at the SPE International Symposium on Oilfield Chemistry in San Antonio, Texas, 14-17 February, 1995.
- Wolery, T.J. (1992a): EQ3/6, A software package for geochemical modeling of aqueous systems: package overview and installation guide (Version 7.0) UCRL-MA-110662 Part I.; Lawrence Livermore National Laboratory.
- Wolery, T.J. (1992b): EQ3NR, A computer program for geochemical aqueous speciation-solubility calculations: theoretical manual, user's guide, and related documentation (Version 7.0) UCRL-MA-110662 Part III; Lawrence Livermore National Laboratory.
- Wolery, T.J. and Daveler, S.A.(1992): EQ6, A computer program for reaction path modeling of aqueous geochemical systems: theoretical manual, user's guide, and related documentation (Version 7.0) UCRL-MA-110662 Part IV; Lawrence Livermore National Laboratory.