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UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
INSTITUTO DE GEOCIÊNCIAS
PROGRAMA DE PÓS-GRADUAÇÃO EM GEOCIÊNCIAS

REVISÃO DE MODELAGEM GEOQUÍMICA E MODELAMENTO GEOQUÍMICO DE RESERVATÓRIO TURBIDÍTICO DA BACIA DO ESPÍRITO SANTO

Marcos Antônio Klunk

ORIENTADOR: Prof. Dr. Rommulo Vieira Conceição

Porto Alegre, Abril de 2017

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RESUMO

A comunidade científica tem presenciado um avanço na modelagem geoquímica para ambientes naturais e hipotéticos. Este desenvolvimento está relacionado com técnicas numéricas capazes de solucionar problemas matemáticos complexos, bem como a melhoria da capacidade de cálculo dos computadores. Embora os conceitos fundamentais da modelagem química tenham evoluído com o tempo, a modelagem geoquímica teve início na década de 60, com os esforços pioneiros de pesquisadores como Garrels et al., (1967) e Helgesson 1967a, 1967b; Helgesson et al., (1968). Devido à complexidade e a escala de tempo envolvido nas reações em ambientes geológicos, não é possível reproduzir em escala laboratorial o comportamento da maioria dos sistemas geoquímicos. A modelagem numérica geoquímica pode ser usada para interpretar e prever os processos que envolvem escalas de tempo não alcançadas em experimentos de laboratório. Embora não seja um substituto para o experimento, a modelagem é uma ferramenta valiosa que pode ser usada para fazer a ligação entre experimentos de laboratório, observações de campo e o comportamento em longo prazo de sistemas geoquímicos. A modelagem geoquímica é uma ferramenta utilizada para simplificar as reações diagenéticas existentes em ambientes deposicionais. A aplicação direta da modelagem geoquímica está aliada com as características estratigráficas e petrográficas da bacia sedimentar. Desta forma, procura-se apresentar um arcabouço com o objetivo de adequar a interpretação exploratória segundo a visão da estratigrafia de sequências, a partir da integração entre sísmica, perfis elétricos, dados de poços e paleontologia. O reservatório selecionado para este estudo está situado na província de domos de sal da Bacia do Espírito Santo, na altura da Foz do Rio Doce, respectivamente a cerca de 40 km da costa. O intervalo corresponde à Formação Urucutuca, constituída por lutitos e arenitos depositados em complexos sistemas de canais entrelaçados, na base do talude, ao longo de calhas geradas pelo diapirismo de sal. As simulações foram destinadas a modelar o efeito da incursão de salmouras, provenientes das proximidades do domo de sal, no reservatório durante a fase de mesodiagênese termobárica. Para formulação do modelo conceitual e configurar as simulações, dados petrográficos simplificados, considerando as fases minerais mais relevantes, foram utilizados para reconstituir as composições dos arenitos durante cada fase da história diagenética. A temperatura utilizada nas simulações é baseada na evolução da história térmica e de soterramento dos reservatórios. Composições de águas dos poços analisadas em laboratório desempenharão o papel das salmouras nos modelos. Para os dados de composição mineralógica dos lutitos e de composição química da provável água de formação, deslocada pela incursão da salmoura, foram utilizadas as informações disponíveis de um provável análogo, os reservatórios turbidíticos da Bacia do Golfo do México. Para a modelagem geoquímica foram utilizados os softwares Geochemist's Workbench – GWB® (Bethke, 2002), TOUGHREACT (Xu & Pruess 1998; Pruess, 1991; Sonnenthal et al., 1998, 2000, 2001; Spycher et al., 2003a; PETRASIM 5) e PRHEEQC (Parkhurst *et al.,* 1999) Os resultados mostram que os lutitos comportam-se como um sistema de interação rocha-fluido dominado pelos minerais, ao contrário dos arenitos, onde os fluidos dominam basicamente devido à diferença de tamanho dos grãos e, portanto de superfície específica para as reações. As simulações executadas revelaram o potencial dos simuladores em modelar situações complexas da diagênese de reservatórios turbidíticos clásticos, bem como a necessidade de integrar dinamicamente a diagênese dos lutitos associados com a dos arenitos para que se possa alcançar resultados coerentes com os padrões diagenéticos reais.

SUMÁRIO

ESTRUTURA DA TESE:

Esta tese de Doutorado está estruturada em torno de artigos publicados e submetidos à revisão em periódicos científicos. Consequentemente, sua organização compreende as seguintes partes principais:

a) Introdução sobre o tema e descrição do objeto da pesquisa de Doutorado, onde estão sumarizados os objetivos e a filosofia de pesquisa desenvolvida, o estado da arte sobre o tema de pesquisa, seguidos de uma discussão integradora contendo os principais resultados e interpretações.

b) Artigos publicados em periódicos ou submetidos a periódicos com corpo editorial permanente e revisores independentes, escritos pelo autor durante o desenvolvimento de seu Doutorado.

1. INTRODUÇÃO

REVISÃO DE MODELAGEM GEOQUÍMICA E MODELAMENTO GEOQUÍMICO DE RESERVATÓRIO TURBIDÍTICO DA BACIA DO ESPÍRITO SANTO

1.1 Contextualização

A modelagem geoquímica é uma ferramenta utilizada para simplificar as reações diagenéticas existentes em ambientes deposicionais. A complexidade observada neste ambiente inclui processos diagenéticos responsáveis pela heterogeneidade dos reservatórios. Na diagênese ocorrem processos físicos, químicos e biológicos pós-deposicionais, nos quais o sedimento, em interação com a água intersticial, sofre diversas reações físico-químicas, numa tentativa de alcançar o equilíbrio com o ambiente (Burley et al., 1985).

A aplicação direta da modelagem geoquímica está aliada com as características estratigráficas e petrográficas da bacia sedimentar. Desta forma, procura-se apresentar um arcabouço com o objetivo de adequar a interpretação exploratória segundo a visão da estratigrafia de sequências, a partir da integração entre sísmica, perfis elétricos, dados de poços e paleontologia.

Nesta tese de doutorado foi estudada a bacia sedimentar Espírito Santo, localizada ao longo do litoral centro-norte do estado do Espírito Santo e o litoral do extremo sul do estado da Bahia, na altura da Foz do Rio Doce a cerca de 42 km da costa. O reservatório produtor de gás corresponde a turbiditos terciários e as acumulações são controladas pela movimentação halocinética observada na região. A Sequência deste reservatório representa o pacote sedimentar assentado sobre a discordância do Pré-Eoceno Superior, mapeável regionalmente na Bacia. Depositada durante o período de quiescência tectônica onde o input siliciclástico foi governado por erosão dando origem a um grande sistema de reservatórios turbidíticos que na atualidade é importante prospecto na Bacia do Espírito Santo. O reservatório é formado predominantemente por corpos arenosos acanalados depositados no trato de mar baixo. A fonte de seus sedimentos consistiu predominantemente de arenitos retrabalhados de sequências subjacentes.

Dados petrográficos desta bacia, coletados pelo laboratório de Mineralogia e Petrologia da Universidade Federal do Rio Grande do Sul sugerem uma história diagenética dividida em quatro estágios: eodiagênese marinha, eodiagênese meteórica; mesodiagênese compactacional e mesodiagênese termobárica (Galloway 1984). Estes quatro estágios correspondem a períodos geológicos caracterizados, cada um deles, pela predominância de processos e controles diagenéticos que os diferenciam.

O estágio eodiagenético marinho foi caracterizado pela precipitação de pirita e carbonatos. O estágio eodiagenético meteórico é registrado pela intensa dissolução e caulinização de grãos silicáticos, em sua totalidade, feldspatos detríticos. A mesodiagênese compactacional é caracterizada por carbonatos autigênicos, silicificação de grãos (tipicamente intraclastos lamosos) e provavelmente, de forma incipiente e algum volume de crescimento de quartzo. Fluxo de fluido conatos modificados oriundos dos lutitos circundantes dentro da sequência caracteriza este ambiente. O último estágio, mesodiagênese termobárica, foi controlado pelos efeitos da percolação de salmouras próximos aos reservatórios turbidíticos.

O poço, situado numa parte dessa Bacia, que corresponde à Formação Urucutuca, e caracteriza por uma acumulação predominante de gás e pequeno volume de óleo, armazenados nos reservatórios turbidíticos arenosos estruturados desta Bacia, contra um domo de sal. Esta formação ocorre devido à flutuabilidade relativa do sal quando soterrado abaixo de outros sedimentos. O sal flui ascendentemente formando um domo salino. Hidrocarbonetos são encontrados geralmente em torno desta formação, devido à abundância de “armadilhas” criadas pelo movimento do sal, e associado com os minerais evaporíticos podem selar a estrutura.

De posse de dados estratigráficos e petrográfico foi possível criar um modelo conceitual, o qual é um modelo capaz de simplificar a realidade deposicional da bacia sedimentar de forma que seja modelado experimentalmente ou através de processos computacionais. Para isso, existem no mercado diversos simuladores capazes de formular modelos geoquímicos prevendo as reações diagenéticas.

Os softwares de simulação utilizaram os modos Batch (sistema fechado constituído de um único volume espacial onde não é permitido fluxo de componentes) e 1D (envolve a interação de fluidos com o meio geológico permitindo a entrada e saída de componentes através de um fluxo contínuo). Estes softwares geralmente são projetados de uma forma genérica, sendo utilizado para recriar qualquer ambiente deposicional. Para a modelagem geoquímica do estágio da diagênese de interesse foram utilizados os softwares Geochemist's Workbench – GWB®, TOUGHREACT e PRHEEQC.

1.2 Problema Científico

Um sistema petrolífero é um ambiente físico-químico dinâmico de geração, migração e armazenamento de petróleo. Inicialmente, o petróleo é gerado em uma rocha rica em matéria orgânica que tenha sofrido um processo de maturação a determinada profundidade (rocha geradora). A seguir, esse petróleo precisa migrar até encontrar litologias que sirvam para armazená-lo e retê-lo na rocha-reservatório através de uma rocha selante, definida como uma rocha que possui características permo-porosas muito reduzidas, o que dificulta a passagem dos hidrocarbonetos (Magoon et al., 1994; Gluyas et al., 2004).

Ao contrário de uma rocha selante, uma rocha-reservatório é caracterizada por ter alta permo-porosidade, ou seja, poros em quantidade suficiente para armazenar o petróleo e boa interconectividade entre eles (permeabilidade). Estas rochas podem ser carbonáticas (Roehl et al., 1985) ou siliciclásticas (Barwis et al., 1990). Os processos diagenéticos mais comuns que afetam uma rocha-reservatório siliciclástica são: calcitização, zeolitização, dissolução, caulinização, albitização, dolomitização, recristalização e cloritização (Tucker, 2001). Se precipitados em quantidades suficientes, esses minerais diagenéticos formam cimentos e obstruem os poros, comprometendo as características permo-porosas da rocha, tornando-a inviável como reservatório. Porém, também há a possibilidade de dissolução posterior de cimentos diagenéticos, gerando porosidade secundária, como acontece em muitos reservatórios.

Os processos diagenéticos permitem que uma variedade de minerais diagenéticos ocorra como cimento nas rochas sedimentares. Como cimento entende-se a precipitação e o desenvolvimento de minerais nos poros das rochas (Worden et al., 2003). Os cimentos mais comuns são: i) quartzo na forma de crescimentos secundários (overgrowths) e microcristais intergranulares; ii) k-feldspato diagenético como crescimentos secundários (overgrowths) ao redor de grãos detríticos ou como cristais discretos preenchendo poros; iii) carbonatos do tipo calcita e dolomita, siderita e mais raramente anquerita, rodocrosita e magnesita; iv) argilominerais como caulinita, ilita, clorita e os interestratificados (especialmente ilita-esmectita. A esmectita também é verificada como cimento, porém, é menos abundante. Os argilominerais são volumetricamente menos significativos, mas extremamente importantes, pois ocorrem como cimentos ou franjas ao redor de grãos, exercendo enorme influência na permo-porosidade da rocha, prejudicando a qualidade do reservatório (Houseknecht et al., 1992). Os fenômenos químicos são os mais comuns e diversificados da diagênese, compreendendo reações que geralmente resultam na precipitação dos minerais autigênicos (Silva, 1991). Do ponto de vista geoquímico, essas reações acontecem porque os constituintes dos sedimentos estão sempre tentando alcançar o equilíbrio e, por isso, tendem a interagir com fluidos intersticiais através de uma soma de processos diagenéticos (Burley et al., 1985). Desta forma, os processos diagenéticos podem ser controlados não só pela temperatura (T), pressão (P) e assembleia mineralógica original, como também pelas atividades dos íons dissolvidos nas águas de formação, Eh (potencial de oxirredução) e pH (atividade dos íons hidrogênio), além da interação com os sistemas orgânicos.

Galloway (1984) estabelece três regimes hidrológicos principais para as águas de formação, relacionados à movimentação e local de ocorrência destas águas em uma bacia: i) regime meteórico, caracterizado nas porções mais rasas da bacia, onde a água presente nos sedimentos é oriunda de infiltração superficial até o lençol freático e pode atingir até 2 km de profundidade; ii) regime compactacional, relacionado à expulsão da água dos poros em função da compactação; iii) regime termobárico ou abissal, associado às partes mais profundas da bacia, onde o fluido intersticial pode ser gerado a partir da desidratação de alguns argilo-minerais e sais.

Considerando a hipótese de que é possível modelar as fases diagenéticas existentes em um arenito reservatório para prever a qualidade dos mesmos como um potencial acumulador de óleo ou gás, a modelagem geoquímica aplicada à bacia do Espírito Santo permite prever as reações diagenéticas existentes neste ambiente deposicional. Estas reações impactam diretamente na quantidade e qualidade do reservatório no cenário da exploração de hidrocarbonetos. Desta forma sabendo a porosidade e permeabilidade, adquiridos pela modelagem geoquímica, é possível estimar a integridade do reservatório.

1.3 Análise Integradora

A ordem dos artigos publicados segue uma sequência de estudos e aplicações.

a) **Artigo 1:** *Application of geochemical modeling software as a tool to predict the diagenetic reactions between marine connate water and the salt dome existing in a petroleum system.* ***Applied Geochemistry*** *(Revisions being processed).*

Abstract

The field of geochemical modeling has grown rapidly since the early 1960s when the first attempt was made to predict the concentrations of dissolved species in seawater. Today's main challenges would be addressed by using geochemical modeling programs to predict the quality of petroleum reservoirs. Therefore, new technologies have been employed for this purpose. The numerical modeling of transport and reaction was used for the understanding of the evolution of the diagenetic processes and their importance in the characterization and prediction of oil reservoir quality (Meshri & Ortoleva 1990; Brenner et al., 1991). Several research groups tried to develop numerical codes for geochemical modeling with and without success. The critical factors for this use are (i) verification of the simulation results with empirical data set and (ii) sensitivity analysis of these results, for the construction of general models which provide a predictive character. This last factor is particularly the most important as it establishes the qualitative and quantitative impact of each parameter in the simulations. Thus, with complete diagenetic numerical model, it is possible to perform various simulations modifying one or another parameter to test the sensitivity in the construction of these different geological scenarios. This set includes mineral composition and texture, composition of fluids, paragenetic sequence and burial history. This work brings fundamental concepts related to this topic as well as an analysis of commercial software and the usage of them to the oil/gas industry on the prediction of reservoir quality. In this context, we analyzed the following software of geochemical modeling: PHREEQC, GWB and TOUGHREACT in batch and generate 1D models with the software GWB and TOUGHREACT. In this study, we modeled the interaction of a marine connate water with a turbidite reservoir in petroleum system of Gulf of Mexico, using the software PHREEQC, GWB and TOUGHREACT. Through compaction and a system of frissures in the sandstone, this brine is expelled from the salt dome reaching the reservoir. The high salinity and the concentration of the solutes induce diagenetic modifications in the sandstones. The scenario chosen for simulations was described in detail by Willson & Fredrich (2005). These interactions affect the diagenetic reactions existing in the sandstone and change the quality of this reservoir.

O objetivo principal deste ***"Artigo 1"*** é a fazer uma revisão bibliográfica dos principais softwares de modelagem geoquímica existentes no mercado e utilizar o PHREEQC, GWB e o TOUGHREACT em um estudo de caso. O senário escolhido foi um sistema petrolífero do Golfo do México onde recriamos a interação de uma água conata marinha com reservatório de arenitos turbidíticos da região. Através do modelamento geoquímico foi possível reproduzir as reações diagenéticas. Um sistema de fissuras e devido ao fenômeno da compactação, expeliram a salmoura, proveniente do domo salino, entrando no reservatório turbidítico. Além dos simuladores serem capazes de prever as reações diagenéticas, os resultados serviram de comparativo mostrando as tendências dos perfis gerados em cada gráfico. As faixas de temperatura ideais nos mostram a estabilidade do método numérico de cada software juntamente com a convergência de resultados quando os minerais atingem o índice de saturação positivo ocasionando sua precipitação.

b) **Artigo 2:** *Formation of magnesite through brine-CO_2 interaction as an important method for CO_2 sequestration: geochemical experiment and modeling.* ***Brazilian Journal of Geology*** *(Revisions being processed).*

Abstract

Burning fossil fuels, which provides more than 85% of the world energy, is one of the largest source of carbon dioxide emission into the Earth's atmosphere (IPCC, 2011; Olivier et al.,2013). Recently, several mitigation techniques have been studied, including injections of carbon dioxide in mature or depleted oil reservoirs and deep saline aquifers (Bachu, 2008; Lemieux, 2011). This work aims to store CO_2 in a mineral form, through the magnesium carbonation of a synthetic solution obtained from an evaporite rock - Bischofite, a hydrous magnesium chloride – (Drijkoningen et al., 2011). This work simulates the proper conditions for trapping CO_2 geologically (Altman et al., 2014; Mitchell et al., 2010). All the results were analyzed by Scanning Electron Microscopy (SEM), Elemental Analyzer CHN X-Ray Diffraction (XRD) and Infrared Spectroscopy (FTIR). Our experiments resulted in the crystallization of magnesite, which is better crystallized at neutral conditions (pH 6.9) in few hours of experiments. However, at longer runs, magnesite became slightly soluble due to the competition between the magnesite formation and dissolution equilibria, and the formation of species slightly acids, such as $H_2CO_{3(aq)}$ and $HCO_3^-{}_{(aq)}$. In order to model our experiment and test the results for natural conditions, we used the TOUGHREACT (version 2.0), Geochemist's Workbench® (GWB version 9.0) and PHREEQC (version 3.0.6) software in "Batch Model" to follow the precipitation of magnesite through the interaction of the species from the aqueous phase to the gas (CO_2) phase, considering the kinetics of the reactions.

O ***"Artigo 2"*** tem como objetivo utilizar um experimento de laboratório e comparar os resultados com o modelamento geoquímico. A interação de $CO_{2(g)}$ com uma solução super-salina (*brine*) resultou na precipitação de carbonato de magnésio (magnesite). Experimentalmente foi possível provar o aprisionamento do $CO_{2(g)}$ em uma fase mineral altamente estável. Com o auxílio do modelamento geoquímico foi possível prever a precipitação de magnesita e outras fases do sistema Mg-carbonatos. O que se conclui que o modelamento geoquímico coincide com a parte experimental. Novamente foi possível verificar o comportamento dos simuladores e suas discrepâncias devido ao método numérico utilizado na temperatura de simulação (120°C).

c) **Artigo 3:** *Geochemical Modeling of Diagenetic Reactions in Snorre Field Reservoir Sandstones: A Comparative Study of Computer Codes.* ***Brazilian Journal of Geology,*** *v. 45, p. 29-40, 2015.*

Abstract

Diagenetic reactions, characterized by the dissolution and precipitation of minerals at low temperatures, control the quality of sedimentary rocks as hydrocarbon reservoirs. Geochemical modeling, a tool used to understand diagenetic processes, is performed through computer codes based on thermodynamic and kinetic parameters. In a comparative study, we reproduced the diagenetic reactions observed in Snorre Field reservoir sandstones, Norwegian North Sea. Baccar & Fritz (1993) modeled these reactions using DISSOL-THERMAL code. In this study, we model the diagenetic reactions in the reservoirs using Geochemist's Workbench (GWB) and TOUGHREACT software, based on a convective-diffusive-reactive model, and on the thermodynamic and kinetic parameters compiled for each reaction. TOUGHREACT and DISSOL-THERMAL modeling showed dissolution of quartz, K-feldspar and plagioclase in a similar temperature range from 25 to 80°C. In contrast, GWB modeling showed dissolution of albite, plagioclase and illite, and precipitation of quartz, K-feldspar and kaolinite in the same temperature range. The modeling generated for temperatures of 100, 120 and 140°C, by the different software show similarly the dissolution of quartz, K-feldspar, plagioclase and kaolinite, but differ in the precipitation of albite and illite. At temperatures of 150 and 160°C GWB and TOUGHREACT produce results different from the DISSOL-THERMAL, except for the dissolution of plagioclase and kaolinite. The comparative study allows choosing the numerical modeling software which results are closer to the diagenetic reactions observed in the petrographic analysis of the modeled reservoirs.

O ***"Artigo 3"*** faz um estudo de caso das reações diagenéticas observadas em um arenito reservatório do campo de Snorre, Mar do Norte Norueguês. Este local foi muito estudado pela comunidade científica onde seus dados estratigráficos e petrográficos estão disponíveis na literatura. Isto possibilitou um estudo comparativo dos modelos gerados pelos GWB e TOUGHREACT com os resultados de um simulador (DISSOL-

THERMAL) que recriou os eventos diagenéticas em várias temperaturas. Os resultados deste estudo comparativo revelaram, mais uma vez, a influência da temperatura nas simulações. O método numérico utilizado por cada software é o responsável pelas discrepâncias observadas nos perfis dos índices de saturação dos minerais. O que se concluir que o usuário precisa ter cautela na escolha de um determinado simulador para recriar as reações diagenéticas em um ambiente geológico com variação de temperatura.

d) **Artigo 4:** *Geochemical Modeling of Burial Diagenesis in Turbidite Reservoirs from the Espírito Santo Basin (Eastern Brazil).* ***Sedimentology*** *(Revisions being processed).*

Abstract

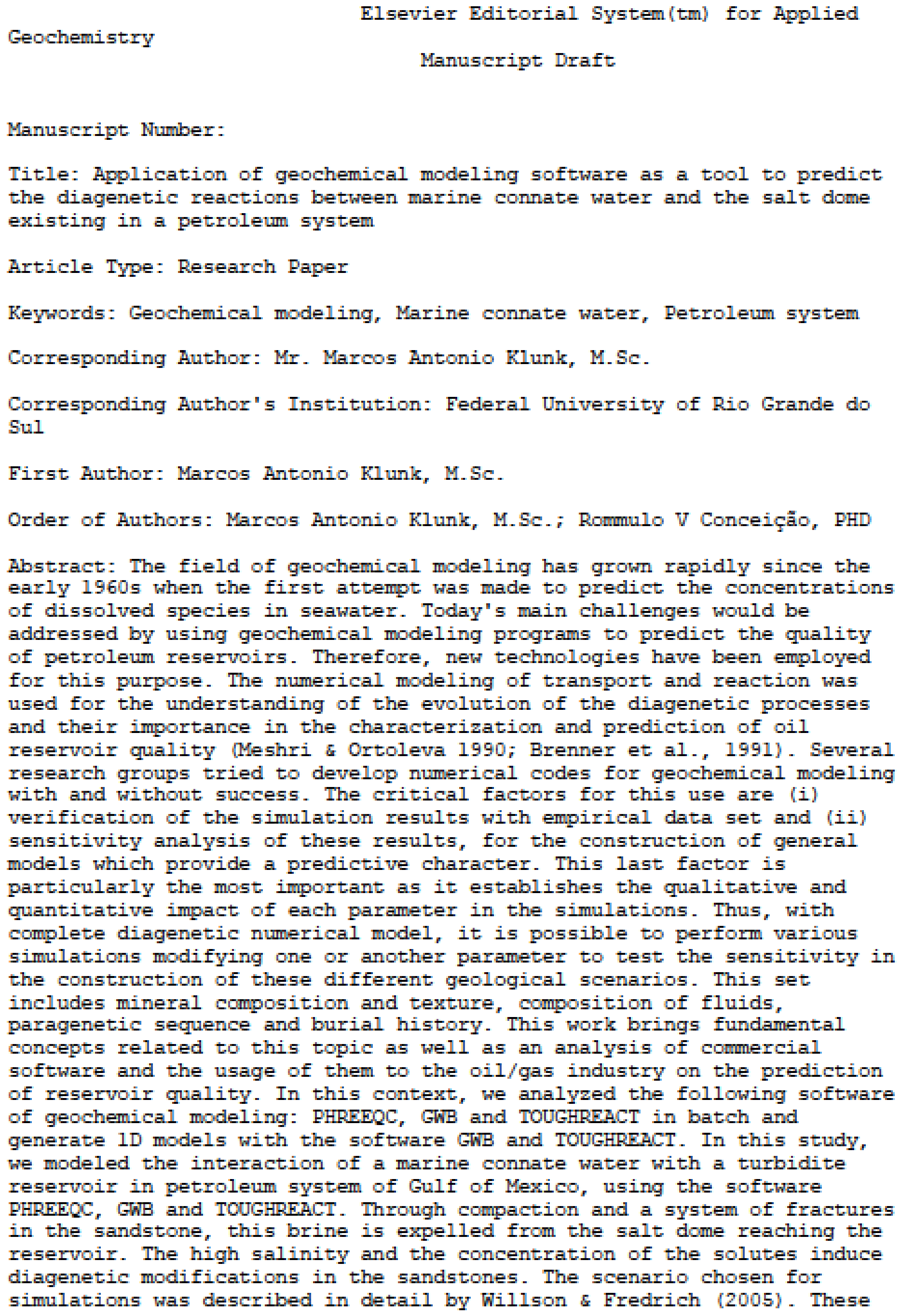
Diagenetic reactions control the quality of hydrocarbon reservoirs. Geochemical modeling, a useful tool to understand the diagenetic processes, can be performed through computer code based on thermodynamic and kinetic parameters. We performed a comparative study of the diagenetic reactions observed in turbidite reservoirs from the Espírito Santo Basin, using the Geochemist's Workbench (GWB), PHREEQC and TOUGHREACT software. The results allowed the comparison of the geochemical modeling with the petrographic observation of dissolution, albitization and kaolinization processes, as well as the precipitation of calcite and dolomite. The porosity of the sandstones can be predicted in relation to the distribution of dissolution, kaolinization and albitization of feldspars, which significantly changed the essential composition of some samples.

O “Artigo 4” utiliza o modelamento geoquímico para prever as reações diagenéticas observadas em um reservatório turbidítico da bacia do Espirito Santo e uma correlação com os eventos diagenéticos observados nas lâminas delgadas (De Oliveira et al., 2013). A análise petrográfica do reservatório sugere uma história diagenética dividida em quatro estágios principais: eodiagênese marinha, eodiagênese meteórica, mesodiagênese compactacional e mesodiagênese termobárica (Galloway 1984). O estágio eodiagenético marinho foi caracterizado pela precipitação de pirita e carbonatos. No estágio eodiagenético meteórico ocorre dissolução e caulinização de grãos, particularmente dos feldspatos e das micas. Na mesodiagênese compactacional verifica-se precipitação de carbonatos e crescimentos de quartzo. O estágio de mesodiagênese termobárica é caracterizado pela percolação de água salgada proveniente de lutitos situados próximas aos reservatórios turbidíticos, oriundos de um domo salino. Com isso, uma vez que se tenha o modelo numérico diagenético completo, é possível realizar diversas simulações modificando apenas um ou outro parâmetro para testar a sensibilidade destes na construção de diferentes cenários geológicos. Este conjunto inclui, por exemplo, composição mineral e textural, composição dos fluidos, sequência paragenética e história de soterramento e de fluxo. Utilizando os softwares de modelagem geoquímica como PHREEQC, GWB e TOUGHREACT. Os resultados obtidos permitiram fazer um comparativo da modelagem geoquímica com a observação das laminas petrográficas (De Oliveira et al., 2013). Tanto na modelagem via software como na petrografia é possível ver os processos de albitização e caulinização, bem como a precipitação de calcita e dolomita. A presença de quartzo diagenético é comum nos arenitos estudados, ocorrendo como crescimentos descontínuos cobrindo os grãos, e como cicatrização de grãos de quartzo fraturados. Com esses resultados é possível estimas a porosidade dos arenitos mediante a combinação da dissolução, caulinização e albitização de feldspatos que alterou significativamente a composição essencial de algumas amostras.

Nota: As referências citas nos itens: "***1.1 Contextualização; 1.2 Problema Científico e 1.3 Análise Integradora***" estão no final deste documento (página 100) como: ***4. REFERÊNCIAS***.

1.4 Artigos Científicos

Artigo 1 : Applied Geochemistry – Revisions being processed



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Abstract: The field of geochemical modeling has grown rapidly since the early 1960s when the first attempt was made to predict the concentrations of dissolved species in seawater. Today's main challenges would be addressed by using geochemical modeling programs to predict the quality of petroleum reservoirs. Therefore, new technologies have been employed for this purpose. The numerical modeling of transport and reaction was used for the understanding of the evolution of the diagenetic processes and their importance in the characterization and prediction of oil reservoir quality (Meshri & Ortoleva 1990; Brenner et al., 1991). Several research groups tried to develop numerical codes for geochemical modeling with and without success. The critical factors for this use are (i) verification of the simulation results with empirical data set and (ii) sensitivity analysis of these results, for the construction of general models which provide a predictive character. This last factor is particularly the most important as it establishes the qualitative and quantitative impact of each parameter in the simulations. Thus, with complete diagenetic numerical model, it is possible to perform various simulations modifying one or another parameter to test the sensitivity in the construction of these different geological scenarios. This set includes mineral composition and texture, composition of fluids, paragenetic sequence and burial history. This work brings fundamental concepts related to this topic as well as an analysis of commercial software and the usage of them to the oil/gas industry on the prediction of reservoir quality. In this context, we analyzed the following software of geochemical modeling: PHREEQC, GWB and TOUGHREACT in batch and generate 1D models with the software GWB and TOUGHREACT. In this study, we modeled the interaction of a marine connate water with a turbidite reservoir in petroleum system of Gulf of Mexico, using the software PHREEQC, GWB and TOUGHREACT. Through compaction and a system of fractures in the sandstone, this brine is expelled from the salt dome reaching the reservoir. The high salinity and the concentration of the solutes induce diagenetic modifications in the sandstones. The scenario chosen for simulations was described in detail by Willson & Fredrich (2005). These

interactions affect the diagenetic reactions existing in the sandstone and change the quality of this reservoir.

Application of geochemical modeling software as a tool to predict the diagenetic reactions between marine connate water and the salt dome existing in a petroleum system

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Abstract

The field of geochemical modeling has grown rapidly since the early 1960s when the first attempt was made to predict the concentrations of dissolved species in seawater. Today's main challenges would be addressed by using geochemical modeling programs to predict the quality of petroleum reservoirs. Therefore, new technologies have been employed for this purpose. The numerical modeling of transport and reaction was used for the understanding of the evolution of the diagenetic processes and their importance in the characterization and prediction of oil reservoir quality (Meshri & Ortoleva 1990; Brenner et al., 1991). Several research groups tried to develop numerical codes for geochemical modeling with and without success. The critical factors for this use are (i) verification of the simulation results with empirical data set and (ii) sensitivity analysis of these results, for the construction of general models which provide a predictive character. This last factor is particularly the most important as it establishes the qualitative and quantitative impact of each parameter in the simulations. Thus, with complete diagenetic numerical model, it is possible to perform various simulations modifying one or another parameter to test the sensitivity in the construction of these different geological scenarios. This set includes mineral composition and texture, composition of fluids, paragenetic sequence and burial history. This work brings fundamental concepts related to this topic as well as an analysis of commercial software and the usage of them to the oil/gas industry on the prediction of reservoir quality. In this context, we analyzed the following software of geochemical modeling: PHREEQC, GWB and TOUGHREACT in batch and generate 1D models with the software GWB and TOUGHREACT. In this study, we modeled the interaction of a marine connate water with a turbidite reservoir in petroleum system of Gulf of Mexico, using the software PHREEQC, GWB and TOUGHREACT. Through compaction and a system of fractures in the sandstone, this brine is expelled from the salt dome reaching the reservoir. The high salinity and the concentration of the solutes induce diagenetic modifications in the sandstones. The scenario chosen for simulations was described in detail by Willson & Fredrich (2005). These interactions affect the diagenetic reactions existing in the sandstone and change the quality of this reservoir.

Key-words: Geochemical modeling, Marine connate water, Petroleum system

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1. Introduction

In order to understand the evolution of the diagenetic processes and predict the oil reservoirs quality, numerical modeling of transport and reaction can be used. Chemical properties of minerals and their interactions with fluids of different compositions is the basis of this methodology. However, the choice of the computer program and the petrological scenario designed for modeling are still a challenge to achieve the success. In this study, geochemical models are represented by numerical equations based in physical-chemical proprieties of the minerals. Mathematical models allow to simulate the behavior of water-rock interaction, providing a better understanding of the development of diagenetic reactions in time and space and its influence on the quality and variety of hydrocarbon reservoirs. The objective is to generate a conceptual and software tool to assist geologists and geochemists in the exploration and production field in their daily task of assessing exploration risks and reservoir characterization. This work has as purpose to go through some software used in geochemical modeling. To verify the saturation index, was used to the software PHREEQC, GWB and TOUGHREACT to batch simulation; and generate 1D models with the following software GWB and TOUGHREACT. In this study, we modeled the interaction of a marine connate water with a turbidite reservoir in petroleum system of Gulf of Mexico. Through compaction and a system of fractures in the sandstone, this brine is expelled from the salt dome reaching the reservoir. The high salinity and the concentration of the solutes induce diagenetic modifications in the sandstones. The scenario chosen for simulations was described in detail by Willson & Fredrich (2005). These interactions affect the diagenetic reactions existing in the sandstone and change the quality of this reservoir.

2. Geochemical Model Approach

A geochemical model is only useful as a tool for prediction if there is a possibility to validate its results. This is a goal that most often is unattainable by the complexity of natural systems, insufficiency of field data and uncertainties relating to the way how the system will change over time. A simplification of reality should be made in order to treat a model as a tool to estimate the probability that a prediction can be considered true or false (Nordstrom 1994).

The principle of mass conservation needs to be applied in geochemical models. Two categories can classify the models: i) the ones that do not consider the transport process referring only to geochemical reaction or simply "batch models"; ii) the others that consider transport processes and geochemical reactions, which are called models of coupled transport and reactions. Determination of geochemical reactions that predominate in a system, quantification of these results and estimation of the flow rates of groundwater (Parkhurst & Plummer 1993) are examples of applications that use these models. Much software using the geochemical reactions are based on conservation of the total concentration of the components combined with the chemical equilibrium. The choice of which software better conveys the model is a challenge.

3. Simulation Process

The coupled transport model differs from the batch model by adding transport processes mathematical formulas to the chemical reaction ones. It simulates the evolution in the geochemical system as long as time pass and estimate the flow path of the fluid that may be 1, 2 or 3 dimensions. The equation of advection-dispersion-reaction (ADR) describes the mathematical process of reaction and coupled transport within a porous medium with a constant flow rate. One of the problems associated with the concept of ADR is the dispersivity (Scheidegger 1954) that introduce a new approach to the problem of modeling of flow and dispersion of solutes in porous media: statistical stochastic. According to Scheidegger (1954) "particles of a fluid not only move along the flow lines resulting from Darcy's law but are also dispersed to the sides, designated dispersivity", which appears in the equations of motion. Under some statistical assumptions, the dispersivity is constant for porous medium. The three medium constants determine the flow of fluid through the porous medium: porosity, permeability and dispersibility.

Most software allow to calculate the precipitation/dissolution of mineral. The reactions are complexation, ion exchange, redox reactions, etc. The main limitation is the quality and availability of thermodynamic data. Much software have excellent databases of aqueous species and reactions in the mineral phase. The activity of aqueous species is calculated using the Davies and Debye-Huckel equation (Bethke 2008). The equations of Pitzer (Pitzer 1991) are important for understanding the behavior of ions dissolved in natural waters such as rivers, lakes and seawater (Stumm et al. 1996; Snoeyink et al. 1980; Millero 2006). Software that simulate kinetic reactions use different numerical methods for equilibrium systems; therefore these methods are appropriate for a set of algebraic and non-linear differential equations.

4. Software for geochemical modeling

There are many commercially available software to simulate systems and geochemical reactions. Due to a large number of programs we will focus just on three of them PHREEQC, GWB e TOUGHREACT. The software is basically divided into 3 modes of interaction: Geochemical speciation modeling, Geochemical Reaction (Batch Systems) e Coupled Transport and Geochemical Reaction. The following are the characteristics of each mode with their respective software.

4.1. Geochemical speciation modeling

The concept of speciation is applied in many chemical systems in special to aqueous solutions (Graeme et al. 2009). Such solutions include natural water systems such as sea, river, ground and lake waters. The chemical speciation of a system is determined experimentally by analytical methods. The geochemical speciation modeling predicts the stable species and separates them according the charge of the ions, forming intermediate species undetectable by analytical instrumentation. The advantage of geochemical speciation is the determination of the concentration of very diluted intermediate species (Bernhard 1999). The software that do geochemical modelling speciation are Geochemist's Workbench – GWB, MINTEQA2 and PHREEQC and they will be described below:

4.1.1. Geochemist's Workbench – GWB

The GWB was developed by the department of geology at the University of Illinois at Urbana-Champaign in 1978. It is currently marketed by "Aqueous Solutions LLC". GWB uses modules SpecE8® and GSS® in "React Mode" for speciation model. The user set the initial condition (concentration of species) of the geochemical system in thermodynamic equilibrium and GWB starts the calculation and necessary interactions that lead to speciation model. When GWB finishs the simulation, output data is generated. The information contained in this file are temperature, pressure, pH, ionic strength, water activity, mass of solvent, dissolved solids, solution density and mass of the rock. An aqueous species list with all solutes presents in the simulation is formed. The "State Mineral Saturation" of the fluid with the mineral is formed in the system. Three relationships occur: i) mineral and solution are in equilibrium - IS = 1; ii) supersaturation - IS > 1 and iii) under-saturation - IS < 1 (Bethke 2008). The GWB solve the equations using Newton-Raphson method (Helgeson et al. 1981).

4.1.2. MINTEQA2

It is a model of speciation in geochemical equilibrium able to calculate dissolved quantities, adsorbed on the solid or gaseous phase in rebuilding a geological environment. MINTEQA2 includes a broad base of reliable thermodynamic data, which is also accessible called PRODEFA2, an interactive program designed to be executed before the MINTEQA2 with the purpose of creating input files needed for the MINTEQA2. MINTEQA2 uses Debye-Huckel and Davies equations to calculate the activity coefficients (Allison et. al 1991).

4.1.3. PHREEQC

PHREEQC is a software written in C and C^{++}program languages designed to perform a wide range of geochemical calculations. PHREEQC implements various types of models in the aqueous phase: ion association models, models of interaction between the ions using the Pitzer equations (Pitzer 1991) and a model of specific ionic interaction. The PHREEQC is able to (i) calculate the saturation index and speciation (ii) calculate the reactions in "batch model" and transport one-dimensional (1D), mixing solutions, and changing temperature and pressure. PHREEQC uses the Pitzer model for high salinity water that is outside the range of Debye-Huckel theory. The use of the Peng-Robinson equation (Stryjek & Vera 1986) is implemented to calculate the solubility of gases at high pressure. Specific volumes of aqueous species are calculated by the dielectric properties of water and the ionic strength of the solution. The software uses method of numerical integration allowing solution of ordinary differential equations, which can be generalized for the reconstruction of three-dimensional trajectories. In an additional package, the PHREEQCI has a graphical interface for Windows® and can to perform all tasks PHREEQC (Parkhurst et al. 1999).

4.2. Geochemical Reaction (Batch Systems)

Below we show information about the programs used mainly for simulations of processes of geochemical reactions in a batch system:

4.2.1. Geochemist's Workbench – GWB

The activity coefficient is calculated by the equation "B-dot" which is an extension of the Debye Hückel equation, and supplemented by model Harvie-Møller-Weare to highly saline solutions such as brine (Kehew 2001). The saturation index of minerals is calculated using models of Debye and Hückel Harvie-Møller-Weare (Bethke 2002). The GWB applies the concept of chemical equilibrium in two different ways. The first concept, derived from the classical theory of thermodynamics, affirms that equilibrium state is the lowest free energy for a system. The second concept, due to the field of chemistry in aqueous solution, affirms that equilibrium state of reversible and irreversible chemical reactions of a system are equal. The steady state of a system is described as the sum of all geochemical reactions that are taking place within each species dissolved. To solve the equilibrium of an initial system, the GWB determines which reactions are more likely to happen, and to what extent they occur.

4.2.2. SOLMINEQ.88

SOLMINEQ.88 is a geochemical modeling program based on equilibrium and thermodynamically irreversible processes, to understand water-rock interactions and predicts its consequences. This program is useful for modeling geochemical interactions in sedimentary basins and oil reservoirs. SOLMINEQ.88 is written in Fortran-77. It uses the Pitzer equations to perform the calculations of activity coefficients, calculates the pH and solubility of minerals in temperatures from 0 ° to 350 ° C and pressure 1-1000 bar. SOLMINEQ.88 predicts the effects of ion exchange, adsorption/desorption and dissolution/precipitation of solid phases (Kharaka et. al. 1988).

4.2.3. RITZ

RITZ is model that simulates the movement of hazardous chemicals during land treatment of oily wastes. RITZ incorporates the influence of oil in sludge, water movement, volatilization, and degradation of a hazardous chemical. Features include interactive data entry and both graphical and tabular output (Nofziger et al. 1988).

4.3. Coupled Transport and Geochemical Reaction

Below there are information about the mainly used programs for the simulations that consider the transport processes and the geochemical reactions.

4.3.1. CHEMFLO

CHEMFLO simulates the transport of water and chemical products in saturated soils, using the equation of Richards (Diersch 2002). The development of mathematical models makes a prediction of the behavior of contaminants and trends preferred for the flow of water in the soil. Modeling in 1D, uses the finite difference method with implicit and explicit linearization. Richards equation (Diersch 2002) incorporates partial differential equations describing the motion of the water and transport of chemicals. The model includes an algorithm to adjust the balance of mass and depth of wetting. The user can specify a grid size and the desired accuracy (Nofziger et al. 1989).

4.3.2. FEFLOW

FEFLOW is a software to simulate the groundwater flow, mass transfer and heat in porous media. The program uses finite element methods to solve the flow equation groundwater saturated and unsaturated. Darcy's law is applied to calculate saturated groundwater flow, however, in unsaturated groundwater flow the code uses Richards equation (Diersch 2002).

4.3.3. HYDRUS-1D and 2D

It is a software that simulates the flow of water in 1D and 2D solute transport in saturated porous media. The 2D version also includes an algorithm optimized parameters like Levenberg-Marquardt for estimating the hydraulic charge. HYDRUS uses the Richards equation (Diersch 2002) to simulate variably saturated flow and advection-dispersion equations for heat and solute transport. The heat transport equations consider the conduction and convection current. The transport equations predict reactions without chemical equilibrium between solid and liquid phases (Šimůnek and Genuchten 1995; Šimůnek et. al. 2005).

4.3.4. MODFLOW

MODFLOW is the software developed by the U.S. Geological Survey first published in 1984, applied to simulate groundwater flow. The software family includes the MODFLOW: MODFLOW-SURFACT, MS-VMS, MT3D and PATH3D. Mathematically, they use finite difference methods for fluid flow calculations (McDonald and Harbaugh, 1984). MODFLOW uses a modular structure wherein similar program functions are grouped together, and specific computational and hydrologic options are constructed in such a manner that each option is independent of other options. Because of this structure, new options can be added without the necessity of changing existing options. The model may be used for either two- or three-dimensional applications. Input procedures have been designed so that each type of model input data may be stored and read from separate external files.

4.3.5. PHREEQC

In batch-reaction calculations, PHREEQC is oriented toward system equilibrium rather than just aqueous equilibrium. For an equilibrium calculation, all of the moles of each element in the system are distributed among the aqueous phase, pure phases, solid solutions, gas phase, exchange sites, and surface sites to attain system equilibrium. Non-equilibrium reactions can also be modeled, including aqueous-phase mixing, user-specified changes in the elemental totals of the system, and any kind of kinetically controlled reaction. Mole balances on hydrogen and oxygen allow the calculation of pe and the mass of water in the aqueous phase, which allows water-producing or -consuming reactions to be modeled correctly. Temperature effects can be modeled with the reaction enthalpy or with a polynomial for the equilibrium constant. Pressure effects can be simulated by entering molar volumes of solids and parameters for defining the specific volume of aqueous species as a function of temperature, pressure, and ionic strength with a Redlich-type equation (Redlich and Meyer, 1964).

4.3.6. TOUGH2

TOUGH2 is a program used for the numerical simulation of fluids and dimensional heat flow multiphase mixtures of several components in porous and fractured. Its main applicability involves geothermal reservoirs, isolation study of nuclear waste, environmental assessment and remediation, flow and transport in saturated media and aquifers. The TOUGH2 was released in 1991 (Pruess, 1991), providing five different fluid properties in modules called "EOS" (equation of state - EOS1" - "EOS5). The adjectives fluid is described by Darcy's law and, moreover, there is the diffusive mass transport in all phases. The description of thermodynamic conditions is based on the assumption that equilibrium location of all phases. The finite difference is a mathematical expression applied in numeric methods (Narasimhan et al. 1976).

4.3.7. TOUGHREACT

The first version of TOUGHREACT was developed by Xu and Pruess 1998, introducing reactive geochemistry heat flow and multi-phase fluid in TOUGH2 (Pruess, 1991). The TOUGHREACT been enhanced with addition: (i) interaction mineral-water-gas and reactive transport under boiling conditions; (ii) improvements in the model for the activity of aqueous species; (iii) diffusion coefficients of gaseous species calculated function of pressure , temperature and molecular properties; (iv) reactive surface area of the mineral -related or fractured porous media; (v) porosity, permeability due to precipitation/dissolution. The flow parameters are based on the codes TOUGH2 V2, with some extensions (Pruess et al. 1999). For transport, the equations are written in terms of the concentration of total dissolved chemicals. The advective and diffusive process are considered for gaseous and aqueous species. These equations are solved by the Newton - Raphson interaction as implemented in the code TOUGH2 (Pruess 1991).

5. Aplication

Evaporite is found in many hydrocarbon basins around the world. Significant evaporitic deposits exist in the Gulf of Mexico, offshore West Africa and Brazil, in the Southern North Sea, Egypt, and the Middle East. Evaporite deposits are formed from the gradual evaporation and ultimate desiccation of enclosed bodies of salt water. The mineralogy of deepwater in Gulf of Mexico evaporite is 94% halite on average, with the dominant impurity being anhydrite. Other evaporates minerals are sylvite, gypsum and carnalite, which comprise up to a few percentage. The non-salt impurities in evaporites, typically representing up to a few percent mass, are quartz, calcite, dolomite, feldspar and clay minerals.

In order to test the efficiency and reproducibility of the modelling software, we used PHREEQC, GWB and TOUGHREACT software in a geologic petroleum system from Golf of Mexico. For that, we developed a conceptual model (**Fig. 1**) based on the geology context described in Willson & Fredrich (2005). Basically, the system is composed of a salt diapir emplaced in sandstone. Water percolates sandstone after dissolving components of the salt dome.

The aim of the conceptual model is to recreate the reactions that occur in the Gulf of Mexico petroleum system of through fissures that allowed the entry of water with very high concentrations of chloride ions in the sandstones of the turbidite reservoir. This percolation of marine connate water triggers a series of diagenetic reactions enabling thermodynamic and kinetic conditions for the precipitation of halite and sylvite.

These precipitated minerals cause a decrease of porosity and permeability impacting the reservoir quality. In order to predict this type of behavior in reservoirs, we used the geochemical modeling based on diagenetic reactions and thermodynamic parameters. The simulations were performed with PHREEQC, GWB and TOUGHREACT software not only to predict the behavior of minerals but also to compare the results of each simulator in this natural environment. For the batch simulations, PHREEQC, GWB and TOUGHREACT, soon, for the simulations in 1D were used GWB and TOUGHREACT.

5.1 Initial conditions of the simulation

A conceptual model of the geological environment was created based on stratigraphic and petrographic data (Willson & Fredrich, 2005) presented above. The conceptual model is the percolation of a brine through fissures into a turbidite sandstone of the Gulf of Mexico, that consequently alter the diagenetic reactions existing in this geological environment. For the formulation of the conceptual model and the configuration of the simulations, simplified data considering the most relevant mineral phases was used to reconstruct the compositions of evaporates and the sandstone during each stage of diagenetic history. The temperatures used in the simulations are 25, 40, 60, 80, 100, 120, 140, 150 and 160°C based on the evolution of heat and burial history of the reservoir, in which there are several interactions between the rock and formation water at different temperatures (Baccar & Fritz 1993). Marine connate water composition was compiled from Nordstrom et al. (1979), which major element composition is in Table 1.

A study conducted by the "British Petroleum" and the "Sandia National Laboratories" (Willson & Fredrich, 2005) on the found that the most common mineral in the evaporite is halite (NaCl), although, there are other types, such as: sylvite (KCl), carnallite ($KMgCl_3.6H_2O$)and a small percentage of gypsum. We will consider halite and sylvite in this modelling (**Fig. 1**).

The first simulations were performed in "batch" mode to obtain compositions of the initial fluids compatible with the rocks. Typically, the sediments are buried at very low rates while temperature increases slowly. Additionally, fluid flow rates are also quite low, limiting the mass movement of elements through the rocks. However, through millions of years, the waters contained in buried rocks tend to reach chemical equilibrium with the rocks.

The diagenetic reactions are therefore a result of this tendency to a state of equilibrium never really achieved. For this reason, a condition close to a "steady state" is more appropriate to describe the chemical state of the diagenetic rocks and fluids. Batch simulations are used to derive the composition of fluids considering the rock compositions obtained by petrographic and other analytical methods.

Once the water reaches chemical stability with rocks through "Batch" model, it is used for the simulations in 1D. The 1D simulation consists of the modified water and two lithologies: the turbidity sandstone (the reservoir rock) and the evaporites (salt dome). The simulation domain has a length of 100 meters and the numerical resolution cell was always one grid per meter. The first part of the simulation domain consists of 20 m of evaporites, while the others 80 m refer to the sandstone reservoirs (**Fig. 2**). This setting allows us to record two important processes in simulations: (1) the effect of marine connate water (low salinity) with the evaporite, and (2) the interaction of brine (contained in the salt dome) with turbidity sandstone.

The first process allows chemical migration mass from evaporites into the sandstones as the water flows. The second allows the diffusive flux controlled by difference in concentration gradient between the two lithologies. Thus, the complex interaction between the water that moves more slowly and the diffusion mechanism that is faster is considered variable and specific for each solution that creates and maintains the reagent transport system, generated by the chemical instability of the lithologies. We generate 1D models with the following software GWB and TOUGHREACT.

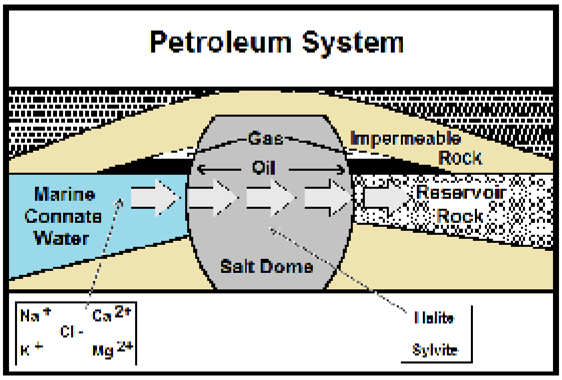

Figure 1: Conceptual model of petroleum system (Willson & Fredrich, 2005). The salt dome is in the direction of turbidite sandstones. Due to fluid mechanic, marine connate water is expelled and migrates into the turbidite reservoirs. The brine rises through the sediments next to the salt dome ceiling, through a network of fractures and reach the reservoir. The high salinity and the concentration of solutes induce diagenetic modifications located in the sandstones.

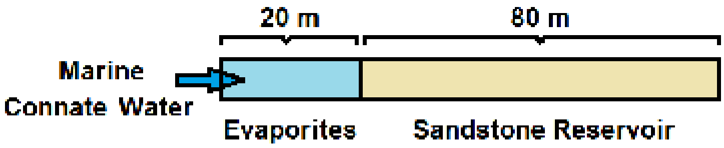

Figure 2: Configuration of the numerical system based on the conceptual model (Fig. 1), One-dimensional domain simulation was generated to test the effect of percolation of the marine connate water in the sandstones.

Table 1: Chemical composition of the formation water (mM/L).

K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	pH
10.45	479.32	10.53	54.39	559.5	8.22

Alkalinity = 2.376 meq/L

Eh = 500 mV

6. Results

6.1. Simulations in "batch" mode

The simulations performed in "batch" mode for 25°C resulted in the graph shown in figure 2, which shows the saturation index of some minerals against time (years). The profiles generated by the simulator reveals the increasing saturation index of halite and sylvite. For halite (Fig. 3A), the PRHEEQC reaches the steady state in approximately 150 years, while GWB and TOUGHREACT steady state is reached after 600 years. Different behavior is observed when sylvite (Fig. 3B) is simulated. The

GWB needs 100 years to stabilize sylvite, while PHREEQC and TOUGHREACT needs need 300 and 700 years, respectively to reach the steady state.

When temperature is changed, variation in the saturation index is observed. Halite (**Fig. 4A**) and sylvite (**Fig. 4B**) saturation indexes are similar for temperature ranges from 25 to 100°C, independently of the software. For higher temperatures (120 - 160 °C), however, each software has a particular numerical method to solve the equations, which consequently generates different curve profiles. In our example, halite suffer from this effect more dramatically than sylvite. It is evident that at low temperatures (25-100 °C) simulators converge independently of the software, in which the thermodynamic and kinetic constants are used without interpolation.

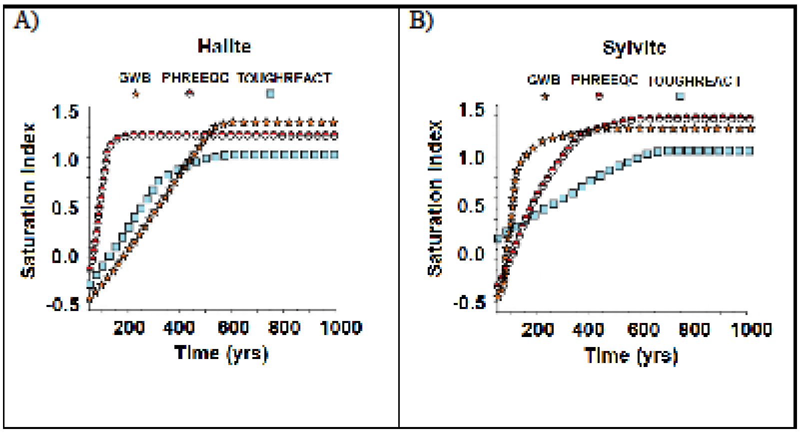

Figure 3: Batch simulations of halite (A) and sylvite (B) with the time in 25°C.

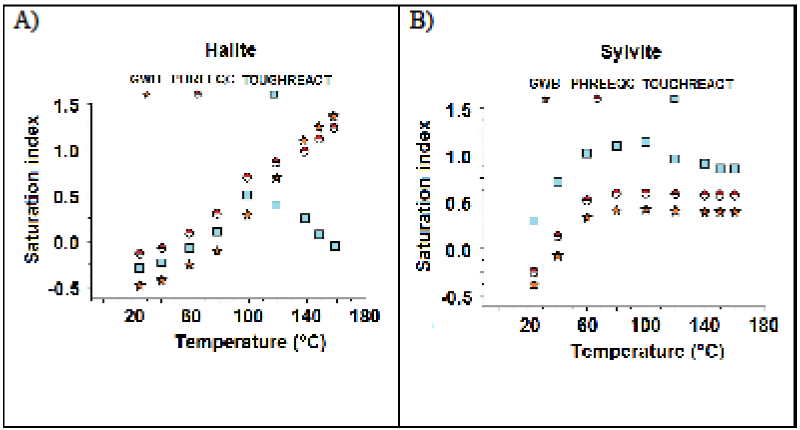

Figure 4: Batch simulations of halite (A) and sylvite (B) with the temperature

6.2. Simulations in 1D

Figures 5A and B show the behavior of halite when the marine connate water percolates the salt dome and enter the sandstone reservoir. Over time, the mineral will reach the "steady state". For 200 years, the reactions are slow, and halite will achieve stability almost at the end of the geological formation (100 m) inside the sandstone reservoir. Over time, the reactions begin to intensify, making the more reactive system, until that halite reaches "steady state" after the 10 meters in the sandstone reservoir.

The same behavior is shown for the two (GWB e TOUGHREACT) software. Each simulator has a different numerical method for calculating the reactions existing in the geological environment. For sylvite (**Fig. 6A** and **6B**) the same trend curves are observed. At the beginning of the simulations, sylvite reacts slowly with sandstone reservoir not reaching the "steady-state". Over the years, the environment becomes more reactive to achieve the stability of the mineral, and again the software reproduced this behavior.

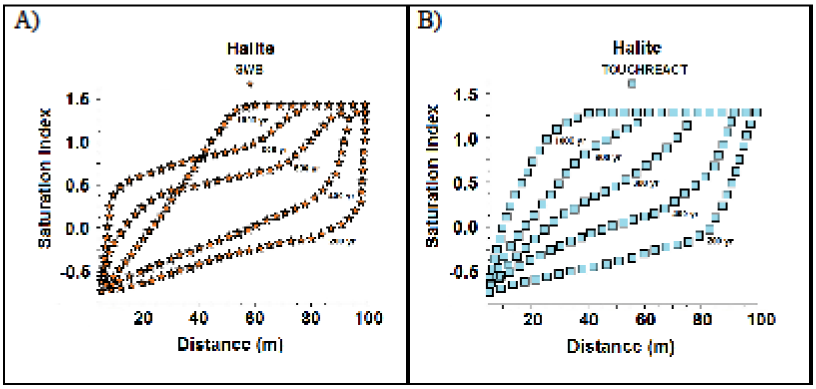

Figure 5: 1D simulations of halite with the distance

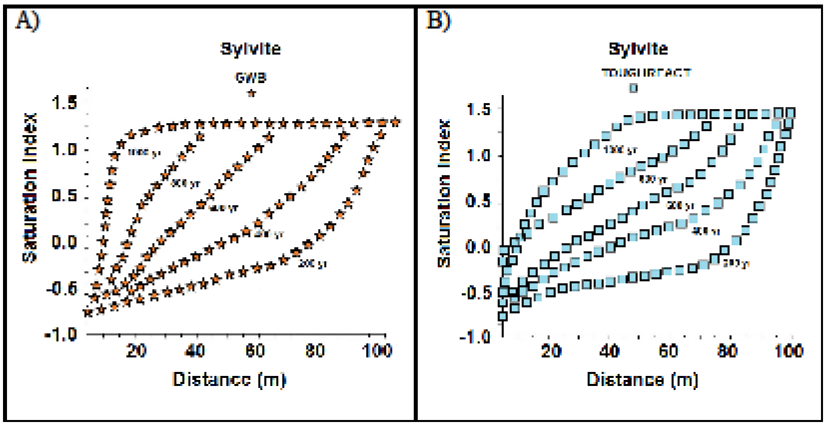

Figure 6: 1D simulations of sylvite with the distance

7. Discussion

The simulations showed a reproducibility of the results using different software of geochemical modeling. Geochemical processes simulated between evaporites and the turbidity reservoir was used to understand the water-rock interactions that would take a thousand years. Thus, the use of software PHREEQC, GWB and TOUGHREACT allowed the modeling.

The simulations in "batch" mode showed the chemical stability of minerals through geological time, and the mineral saturation index variation through temperature. The non-steady state of initial water is a result of the difference between the number of solutes (5) and the number of minerals (2) present in evaporites. Thus, there is a sharing of these minerals with the chemical element causing dissolution, being evident the negative saturation index. Once the simulations advance and the waters are flowing from the salt dome toward the sandstone, reaction fronts begin to form with the waters-rock interaction. Water entering the sandstone by salt dome creates a pattern of different diagenetic alteration of reactions that existed between the steady state marine connate water and sandstones.

The mixture of the water in the sandstone and the water that came from the evaporate led to a new composition of the solutes due to the phenomenon of diffusion of ions into the salt dome toward the reservoir. An immediate consequence is that water is far from equilibrium, as shown by mineral saturation index in the mixing zone according to figures 5 and 6. In 200 years, the minerals deriving from the salt dome is not stable with the sandstones. A new trend reaction occurs, from 400 years, causing a new steady state regime (**Fig.5** and **6**). As shown in the results, the use of different codes produces different results during modeling. In "batch" mode, the GWB, TOUGHREACT and PHREEQC software reproduce similar results at low temperatures due to the use of similar numerical methods and the low kinetic energy involved in the diagenetic reactions. In the physical-chemical approach to lower temperature reactions, the kinetic energy decreases generating similar results.

Each simulator has their algorithms based on mathematical codes that are dependent on kinetic and thermodynamic parameters of each mineral, contained in the database. At higher temperatures ($T>100°C$) the simulation results show some discrepancies because each software uses different numerical methods to solve a different set of reactions. Contrarily, at elevated temperatures (120 to 160°C) there is an increasing in kinetic energy, incrementing the intensity of the reactions, which decreases discrepancies among softwares. GWB, and PHREEQC software generate similar results.

However, TOUGHREACT shows different approaches while working with high temperatures when compared to the GWB and PHREEQC. The behavior of halite can demonstrate this. The numerical method of systems uses polynomial equations of 8th grade to resolve the physical-chemical interactions in geological environments. These equations are dependent on kinetic and thermodynamic data of minerals that form paragenesis in sandstone reservoirs. For temperatures above 120°C, these kinetic and thermodynamic data acquire an anomalous behavior for some minerals, assuming constant values of 500 in eighth-degree polynomial, in the numeric methods, for treating as if not known.

For simulation 1D, this comparative study revealed two stages, taking into account the geologic time and domain of water-rock interactions. The first stage corresponds to the range 0 – 1000 years and the second stage, to the distance range of 0 – 100 meters. In the lower time stage (0 to 200 years) the simulators do not reach the necessary stability for minerals. As time evolves (over 400 years), minerals begin to acquire stability, to achieve stability in 1000 years. As the water moves into the geological formation, the reaction occurs between solutes and minerals. This behavior induces a steady-state of the minerals due to the kinetic energy involved.

Users must be careful when choosing a geochemical modeling software because, depending on the temperature range, different systems can produce very discrepant behaviors. Although the GWB, PHREEQC and TOUGHREACT software reproduce the largest number of similar reactions, users must be cautious in interpreting their data. The choice of the software for geochemical modeling should consider the differences between each code, in a way to reproduce the reactions of the geological environment of interest with a greater approximation of reality.

8. Conclusions

The present study of geochemical modeling comparing the application of GWB, PHREEQC and TOUGHREACT codes for the simulation of reactions observed in the reservoir sandstones with salt dome, resulted in the following conclusions:

1) Modeling at low temperatures (25 to 100°C) with different simulators reproduce similar behaviors in batch mode. In this temperature range, which involves low energy, the reaction kinetics and the thermodynamic parameters has according to the particularities of each code. The numerical methods used by GWB software, PHREEQC and TOUGHREACT can achieve only limited convergence of results, with the high precision expected for reactions at low temperature geological environments.

2) For the range of temperature from 120 to 160°C, the simulations with TOUGHREACT generate discrepancy results when compared with GWB. There is higher kinetic energy involved, and consequently the reactions take place with greater intensity. In this temperature range, water-rock interaction has a very high kinetic energy, causing fast reactions within the geological environments, making the prediction of the reaction less possible. In this way, each simulator seeks each own best set of numerical solutions to achieve the equilibrium.

Users must be cautious when choosing a geochemical modeling software, as an important factor in determining a simulator is to know the temperature range that will be used. With the temperature information, the user should do a preliminary study with the available codes for verifying the convergence of results to the observed diagenetic reactions.

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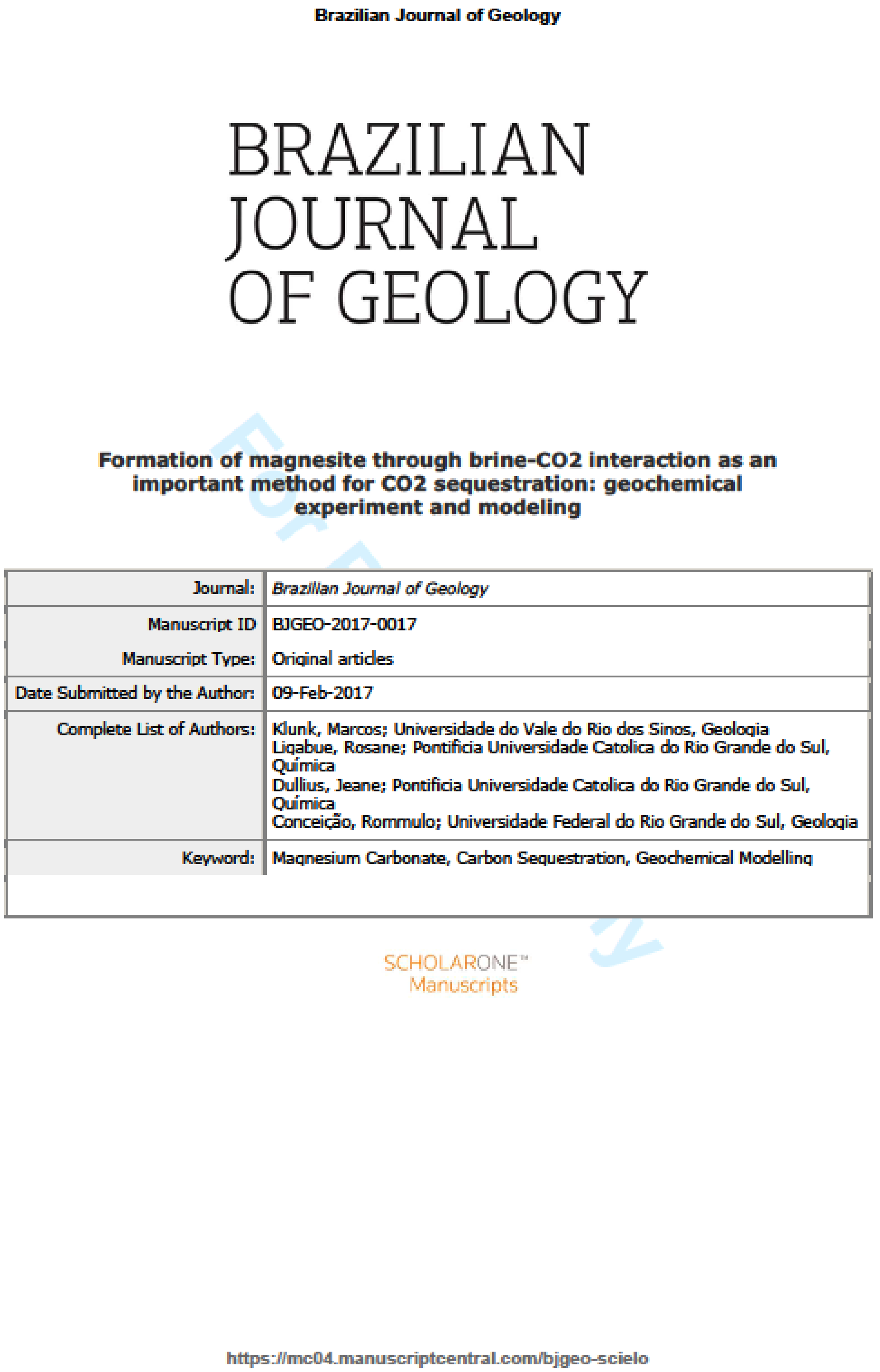

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Formation of magnesite through brine-CO2 interaction as an important method for CO2 sequestration: geochemical experiment and modeling

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Keyword:	Magnesium Carbonate, Carbon Sequestration, Geochemical Modelling

Formation of magnesite through brine-CO_2 interaction as an important method for CO_2 sequestration: geochemical experiment and modeling

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Abstract

Burning fossil fuels, which provides more than 85% of the world energy, is one of the largest source of carbon dioxide emission into the Earth's atmosphere. Recently, several mitigation techniques have been studied, including injections of carbon dioxide in mature or depleted oil reservoirs and deep saline aquifers. This work aims to store CO_2 in a mineral form, through the magnesium carbonation of a synthetic solution obtained from an evaporite rock (Bischofite, a hydrous magnesium chloride). This work simulates the proper conditions for trapping CO_2 geologically. All the results were analyzed by Scanning Electron Microscopy (SEM), Elemental Analyzer CHN X-Ray Diffraction (XRD) and Infrared Spectroscopy (FTIR). Our experiments resulted in the crystallization of magnesite, which is better crystallized at neutral conditions (pH 6.9) in few hours of experiments. However, at longer runs, magnesite became slightly soluble due to the competition between the magnesite formation and dissolution equilibria, and the formation of species slightly acids, such as $H_2CO_{3(aq)}$ and $HCO_3^-{}_{(aq)}$. In order to model our experiment and test the results for natural conditions, we used the TOUGHREACT (version 2.0), Geochemist's Workbench® (GWB version 9.0) and PHREEQC (version 3.0.6) software in "Batch Model" to follow the precipitation of magnesite through the interaction of the species from the aqueous phase to the gas (CO_2) phase, considering the kinetics of the reactions.

Key-words: Magnesium Carbonate, Carbon sequestration, Geochemical modelling

1. Introduction

The burning of coal, oil and natural gas, as well as deforestation and various agricultural and industrial practices are altering the composition of the atmosphere and contributing to climate changes (IPCC, 2011; Olivier et al.,2013).

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These human activities have led to atmospheric concentrations increasing of greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_xO_y hydrofluorocarbons (HCFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF_6). Many researchers are investigating the problem of rising atmospheric CO_2 concentration through various stabilization mechanisms (IPCC, 2011). In an attempt to reduce, or at least slow down, the increase in atmospheric CO_2 levels, several mitigation processes are currently being studied, among which the most promising is the capture and geological storage of carbon (Bachu, 2008; Lemieux, 2011). One of the geological storage methods involves the injection of CO_2 into a deep saline aquifer or into mature or inactive oil reservoirs (Xu et al., 2006; Bachu, 2000). Once underground, a variety of mechanisms keep the CO_2 securely stored: hydrodynamic, solubility and/or mineral trapping. hydrodynamic trapping is the storage of CO_2 either in its gas form or in a supercritical fluid form inside a porous rock underneath another with low permeability. The solubility trapping involves the dissolution of CO_2 in a liquid phase such as brine or oil trapped in a rock. The mineral trapping involves the incorporation of CO_2 into a solid phase, for example, precipitation of carbonate minerals or adsorption on coal surface (Altman et al., 2014; Mitchell et al., 2010). Many scientists refer to mineral trapping as a permanent sequestration of CO_2, as many carbonates remain geologically stable for a long period of time. As mineral carbonation is an efficient way of storing CO_2 indefinitely, it is necessary to study the stability and reactivity of the carbonate chemical systems in the presence of several other ions.

In this work, we investigate the reactivity conditions for carbonate precipitation in a magnesium chloride solution, which simulates an evaporitic solution, when in contact with a supersaturation of CO_2 gas. Our goal is understand the best condition to keep carbonate mineral stable in such system and model all chemical interactions through numerical geochemical modeling. Our experiment emulates the injection of CO_2 gas into evaporitic rocks, which promotes the formation of aqueous solutions of carbonate and bicarbonate. Some of the precipitated carbonates (magnesite, for example) has low solubility in water and should remain stable for thousands or millions of years (Krupp, 2005). Bischofite ($MgCl_2.6H_2O$), an important mineral in evaporitic rocks, was used as a source of a brine composition enriched in Mg in our experiments. Mg-rich brines usually occur in the final stages of the sea water evaporation and bischofite saturation depends mostly on the weather, which must be hot and dry. Magnesium chloride brines also occur as a product of metamorphism, or deep aquifers diagenesis (Drijkoningen et al., 2011).

Due to the complexity and the time scale involved in the reactions in geological environments, it is not possible to reproduce in laboratory the exact behavior of most natural geochemical systems. Numerical geochemical modeling can be used to interpret and predict the processes that involve timescales unreached in laboratory experiments. For this study, we model our experiments using the TOUGHREACT (Xu & Pruess 1998), GWB (Bethke, 2002) and PHREEQC (Parkhurst & Appelo 1999) software in the "batch mode" (closed system and one cell simulation without flux), in order to create the conditions of precipitation and/or dissolution in a carbonate systems.

2. Experimental and Modelling Methods

2.1. Starting Material

Magnesium chloride solutions with different concentrations were prepared from magnesium chloride hexahydrate ($MgCl_2.6H_2O$) MERCK® with 99.99% purity. $CO_{2(g)}$ gas from Martins PRAXAIR INC. WHITE®, with concentration of 5000 ppm packaged in cylinder, with a purity of 99.95% was used in all experiments. The magnesium solution concentrations were obtained by dissolving the $MgCl_2.6H_2O$ in ultrapure water and adjusting the pH to 8.50 – 9.50 with pellets of potassium hydroxide (KOH, 99.99% pure, Merck®). Two concentrations were made: i) 24 $g.L^{-1}$ (100% saline) and ii) 12 $g.L^{-1}$ (50% saline) in Mg^{2+} ions. A calibration curve prepared with standard solution of Mg^{2+} (Merck®/Titrisol) and analysis using Flame Atomic Absorption Spectrometry aided accuracy for these saline solution concentrations.

2.2. Reaction Conditions

All reactions between the Mg^{2+} saline solution and the $CO_{2(g)}$ were performed in stainless steel reactor of 120 mL internal volume in batch condition. The carbonation reactions were conducted under the same reaction temperature (120°C), and initial $CO_{2(g)}$ partial pressure condition (60 bar), but at different run times: 0.5, 1, 2, 3, 4 and 5 hours. The reactions were conducted in a 50 mL fixed volume of reaction medium under two conditions of Mg^{+2} ion concentration: i) R1 Condition: 50% saline (12g $.L^{-1}$ of Mg^{2+}) in pH 7.5; and ii) R2 Condition: 100% saline (24g.L^{-1} of Mg^{2+}) in pH 7.5.

2.3. Characterization of the Material

After the runs, the solution inside the reactor was filtered through previously weighted 0.22 µm membrane (Millipore®) under reduced pressure. After drying at 100°C, the membrane was weighted again on an analytical balance and the mass of precipitated material was obtained. Flame Atomic Absorption Spectrometry (Varian SpectrAA 55®), Elemental Analyzer CHN LECO®, Infrared Spectroscopy (PerkinElmer) and X-Ray Diffraction (Siemens D500) were used for the chemical and structural characterization of the precipitate. The morphology of the precipitate was performed with a Scanning Electron Microscopy (SEM) Philips® model XL 30).

2.4. Geochemical modeling

A large number of programs is used to simulate kinetic reactions in a given geological environment. In order to simulate the reactions of precipitation and/or dissolution in our experiments, we used the TOUGHREACT, GWB and PHREEQC, both in the "batch system".

TOUGHREACT was used with the ECO2N module as the equation of state (EOS), because it involves an interaction of $CO_{2(g)}$ in a saline solution. The equations that govern the module ECO2N have the same structure deriving from the principle of conservation of mass (or energy) assuming a state of equilibrium. The code uses non-isothermals equations (Pruess, 1987; Pruess et al., 1999). The numerical solution to the water-CO_2 interaction uses the discretization of the integral space using integral finite difference (Narasimhan & Witherspoon 1976). These equations are solved by the Newton-Raphson interaction (Pruess, 1991). The activity of aqueous species is equal to the product of the activity coefficient and molar concentration, and the activity coefficient is calculated using the Debye-Huckel equation (Helgeson & Kirkham 1974).

The GWB was developed by the department of geology at the University of Illinois at Urbana-Champaign in 1978. It is currently marketed by "Aqueous Solutions LLC" in three ways: GWB Essentials, Standard and Professional. GWB Professional was used in the “React” module at equilibrium condition in order to simulate the CO_2 and Mg^{2+} solution interaction. Using in this way, GWB performs a series of irreversible (no equilibrium) reactions progress to a state of thermodynamic equilibrium. Equation balance is solved by the numerical Newton-Raphson method. Mass balance is considered during the solution of each equation.

PHREEQC is software written in programming languages C and C++ designed to perform a wide range of geochemical calculations. PHREEQC implements various types of models in the aqueous phase: ion association models, models of interaction between the ions using the Pitzer equations and a model of specific ionic interaction. Use the Pitzer model for high salinity water that is outside range of application of the Debye-Huckel theory. The software use method of numerical integration allowing solution of ordinary differential equations, which can be generalized for the reconstruction of three-dimensional trajectories (Parkhurst & Appelo 1999).

3. Results and Discussion

All reaction conditions and results are listed in the table 1.

3.1 Formation of the precipitate

All experiments resulted in a precipitated material inside the reactor, which was dried, weighted and characterized. In the R1 runs (50% saline system) the amount of precipitate increased from 91.7mg in 0.5 hours run to 148.2mg in 3 hours run. This variation corresponds to 62% of mass increasing compared to the first 0.5 hours of reaction. This mass increasing is in accordance with studies made by Soong *et al.* (2004). For R1 runs performed in 4 and 5 hours there was a mass decreasing from 121.1mg to 114.1mg, respectively, due to the formation of carbonic acid (H_2CO_3) during the reaction (see table 1), which dissolves the previously precipitated carbonate species. In the R2 (saline 100%) runs, a new behavior in the formation of the precipitates was found. The 0.5 to 5 hours runs resulted in 59.2mg to 83.1mg of precipitate, respectively. This mass increasing corresponds to 41%, compared to the amount of mass in the first 0.5 hours. This behavior is different from that described by Soong et al. (2004), because the amount of precipitate continues to increase after 5 hours of reaction. This suggests that the formation of carbonic acid (H_2CO_3) in this time of reaction is not enough to dissolve the previously formed precipitate.

Table 1
Reactions conditions for R1 and R2

Reaction	Time (hours)	Solution final pH	PPT* (mg)	Final concentration Mg^{2+} (g.L^{-1})
R1 – 01	0.5	4.50	91.7	8.20
R1 – 02	1	5.00	127.0	5.54
R1 – 03	2	5.50	138.4	3.51
R1 – 04	3	6.80	148.2	2.00
R1 – 05	4	5.20	121.1	3.12
R1 – 06	5	5.10	114.1	5.10
R2 – 07	0.5	5.21	59.2	14.20
R2 – 08	1	5.55	62.7	13.10
R2 – 09	2	5.82	65.0	12.50
R2 – 10	3	6.31	71.0	11.91
R2 – 11	4	6.52	79.1	9.74
R2 – 12	5	6.90	83.1	8.12

PPT = total material precipitate

3.2. Mg^{2+} ion concentration in solution

Mg^{2+}concentration was determined in the product of each run by filtering the samples through a membrane of 0.22 μm under reduced pressure and determining Mg^{+2} concentration in the solution with a Flame Atomic Absorption Spectrometry. Results are shown in table 1. The reaction condition R1, which initially shows an Mg^{2+}concentration of 12 g.L^{-1}, changed to 8.3% of Mg^{2+} ions in the solution after 3 hours of reaction. Such result corresponds to 91.7% of mineral precipitation. In reaction condition R2, which initially shows a Mg^{2+}concentration of 24 g.L^{-1}, changed to 43% of Mg^{2+} ions in the solution after 5 hours of reaction, which corresponds to 57% mineral precipitation. In all experiments there is magnesium carbonate formation. The variation of pH along the reaction determines which carbonate specie is present in the solution. For reactive systems R1–01, the prevailing pH in the final solution is 4.50, which suggest that carbonic acid (H_2CO_3) predominates in the system as the soluble carbon specie, according to Gerven et al. (2004). Under this condition the previously precipitated carbonate undergoes to a process of dissolution, because in such condition there are larger amounts of free H$^+$ ions (from dissociation of H_2CO_3), which results in more dissolved Mg^{2+} ions in the solution (8.20 g.L^{-1}). In the reactions R1–04, the pH of the final solution is 6.80. This increased pH, compared to the reaction R1– 01, resulted in Mg^{2+} ions decreasing in the solution (2.00 gL^{-1}), which is a consequence of better magnesium carbonate crystallization. In the R2-07 reaction condition, after 0.5 hours run, the final pH is 5.21, which is slightly acidic. In such condition, carbonic acid (H_2CO_3) and bicarbonate ions (HCO_3^-) species coexist in the solution and the Mg^{2+} ion concentration in the solution is 14.20 g.L^{-1}. As far as pH values increase from R2-07 (pH – 5.21) to R2-12 (pH-6.9), Mg^{2+} concentration in the solution decreases, as a result of carbonate precipitation, which suggest the predominance of HCO_3^- species, compared to H_2CO_3 species.

3.3. Characteristic of the precipitate

3.3.1. Infrared spectroscopy

Figure 1 represents the infrared spectrum of two samples of precipitates corresponding to R1-06 (5 hours run) and R2-12 (5 hours run). We compared these spectra with a synthetic magnesium carbonate ($MgCO_3$ extra pure MERCK®), which is shown in Fig. 1.

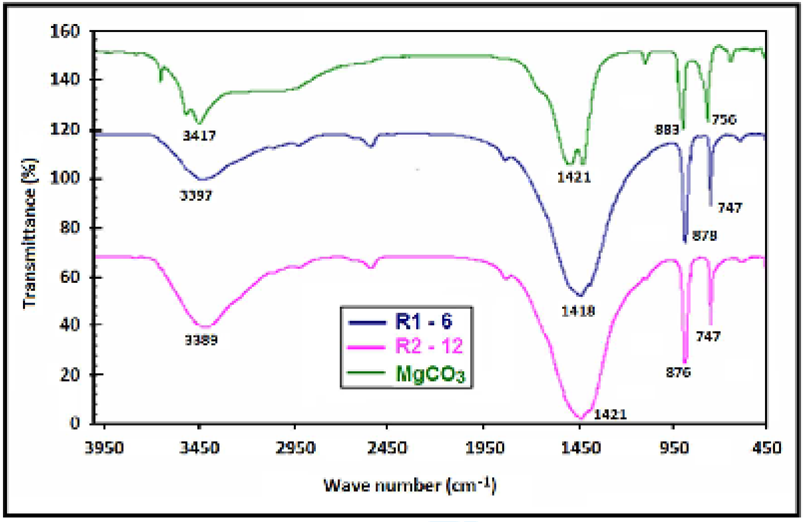


Fig. 1. Infrared spectrum corresponding standard $MgCO_3$ and the two samples of our experiments.

The 3389, 3397 and 3412 cm^{-1} absorption bands correspond to O-H stretching and are attributed to water or hydroxyl containing compounds (White, 1971). A second group of absorption bands appears at 1421, 1418 and 1421 cm^{-1}, which is characteristic of CO_3^{2-} stretching in carbonate compounds. Absorption bands between 883-756, 878-747 and 876-747 cm^{-1} appear for the spectra R1–6; R2–12 and $MgCO_3.5H_2O$, respectively, which correspond to complex structures of Mg-carbonate system (White, 1971).

Samples R1-6, R2-12 and $MgCO_3.5H_2O$ show similar bands in CO_3^{2-} stretchings (1440 and 1420 cm^{-1}) and complex shapes between 870 and 880 cm^{-1}. The results for precipitates of reactions R1 - R2 are similar to those obtained by Oh et al. (1973) for magnesite, and White (1971) for complex forms of Mg-carbonate. Infrared spectroscopy analysis suggest that carbonation occurred in the runs due to the similarities between our spectra and those from the literature (Oh et al.,1973; White, 1971).

3.3.2. Elemental Analysis and X-Ray Diffraction

Elemental analysis CHN (LECO®) detected up to 15% of carbon in the precipitated material in all runs, which is similar to the theoretical carbon amount of anhydrous magnesium carbonates (around 14%). X-ray diffraction analyses (Fig. 2) were performed on all precipitated samples, which confirm magnesite as the main precipitated mineral.

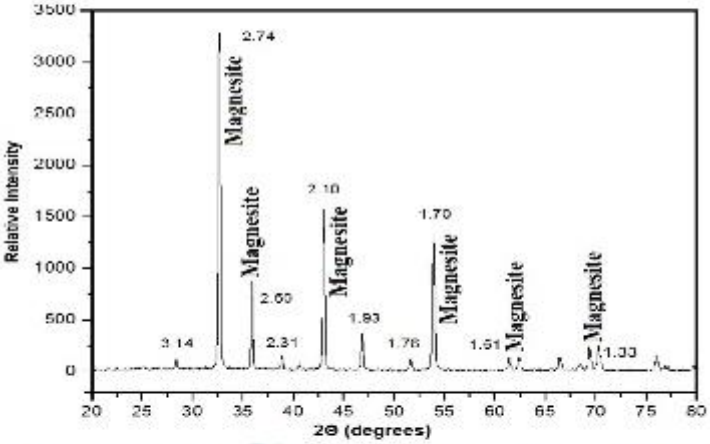


Fig. 2. Characterization by X-ray diffraction of the precipitated containing $MgCO_3$ in sample R1 - 06

3.3.3. *Microstructural Characterization*

Scanning Electron Microscopy (SEM) images (Fig. 3a, 4a) and Spectrometer Energy Dispersive X-ray (EDS) analysis (Fig. 3b, 4b) on the precipitated samples for R-1 reactions suggest that magnesite is the major phase. All SEM images show a rhombohedric phase, which is typical for calcite and magnesite according to Oh et al. (1973), and the magnesium peak is present in all EDS analysis.

Fig. 3a. SEM of the material precipitated from the reaction R1 - 04 (3h)

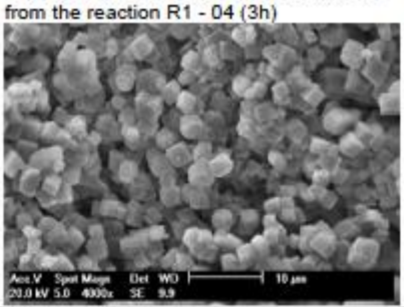


Fig. 3b. EDS precipitated from the reaction R1 - 04 (3h)

Fig. 4a. SEM of the material precipitated from the reaction R2 - 12 (5h)

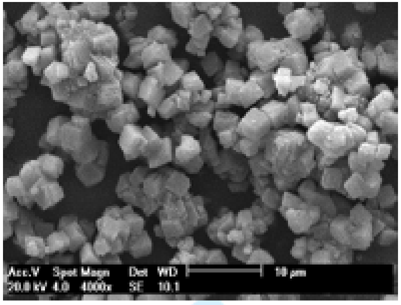
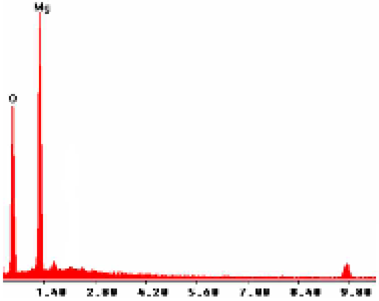


Fig. 4b. EDS precipitated from the reaction R2 - 12 (5h)



3.4. Numerical Modelling of the Experiments

TOUGHREACT, GWB and PHREEQC software simulations were performed for these experiments considering 5 hours in 120°C in R1 and R2 reactions conditions. All simulations were conducted in "batch system" without flux, in order to better simulate the runs. Numerical simulations considered the list of minerals selected in Table 2. Figures 5 and 6 show the simulations in volume fraction of magnesite versus reaction time for these three software. For R1 conditions (Fig. 5) we notice that the volume fraction of precipitated material progressively increase from 0.5 to 3 hours (Fig. 5) and from this moment, dissolution reactions occur, causing decreasing in the volume fraction of magnesite. This phenomenon is characteristic of pH change due to the formation of acid species, leading to magnesite volume loss. The R1 reaction conditions favor the formation of ionic species such as HCO_3^- in such amount that affect the nucleation of magnesite and result in magnesite dissolution. This simulation corroborates what was observed experimentally. Generally the simulation results show some discrepancies depending on the modelling, because each software uses different numerical methods to solve a different set of reactions. However, all chosen numerical modelling are very consistent and converge with this result.

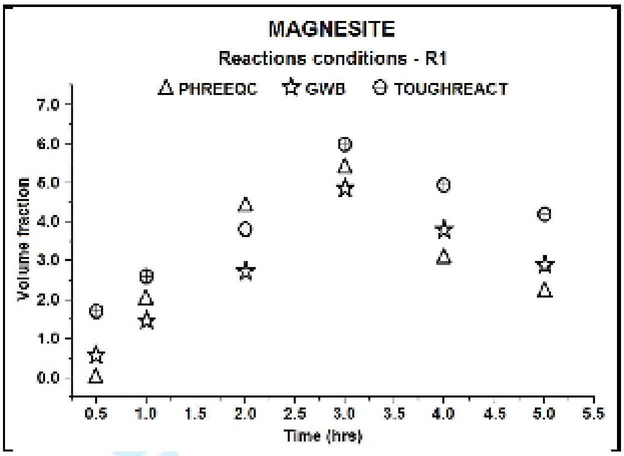


Fig. 5. Geochemical modeling of magnesite in reactions condition R1.

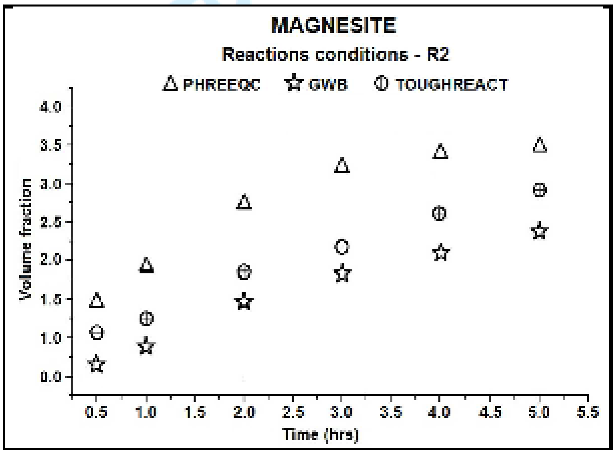


Fig. 6. Geochemical modeling of magnesite in reactions condition R2

In the numerical model for R2 reactions conditions (Fig. 6), we observed a volume fraction increasing from the beginning to the end of 5 hours in our simulations. The R2 reaction conditions show that the concentration of the brine directly affects the formation of magnesite. Under these extreme conditions, acidic species are also produced, but in such small quantities that do not dramatically interfere in the magnesite precipitation reactions. The higher the initial concentration of the brine, greater is the formation of carbonates (magnesite). Again, the three numerical modeling converge in results. The models that describe the volume fraction of these three softwares are equivalent. Knowing that each simulator has different numerical methods, the kinetic energy and thermodynamics parameters are applied satisfactorily, leading to convergent curves profiles. Figures 7 and 8 show the reactions conditions in R1 and R2, respectively, modeled to Mg^{2+} ion concentration versus reaction time. The behavior of Mg^{2+} ions are inversely proportional magnesite formation, as expected.

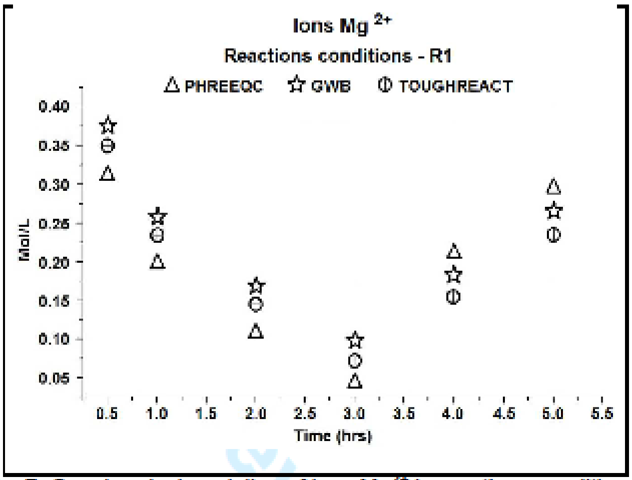


Fig. 7. Geochemical modeling of ions Mg^{2+} in reactions condition R1

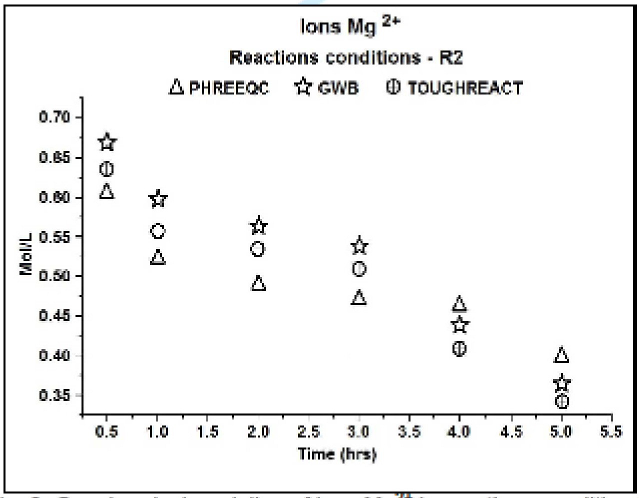


Fig. 8. Geochemical modeling of ions Mg^{2+} in reactions condition R2

An advantage of using mass fraction equation formalism of the geochemical model, adopted by software, is the use of the saturation index (SI) of minerals. The software calculates the product of ionic activity (Q) and compares with the solubility product (Ksp) default values. The calculation of the

SI is performed as i) IS = 1 (minerals and solution is stationary state); ii) IS > 1 (supersaturated); iii) IS < 1 (unsaturated).In Figures 9 and 10 we have proposed models for magnesite saturation index in reaction conditions R1 and R2 respectively. Modeling of the volume fraction and concentration of Mg^{2+} ions is as important as the magnesite saturation index modelling to detect the stationary state of the mineral phase. The three softwares generate very similar models in both reaction conditions. We observed that the steady state is reached faster in R2 (Fig. 10), due to the high concentration of brine. The greater availability of Mg^{2+} ions in the solution favors the kinetic energy of the reaction towards the products. However, at lower concentrations of Mg^{2+} ions, the steady state shifts to higher reaction times (Fig. 9).

Mathematically, GWB and PRHEEQC use finite difference methods to calculate the reactions. The activity coefficient is calculated by the equation "B-dot", which is an extension of the Debye Hückel equation, supplemented by model Harvie-Møller-Weare to highly saline solutions, such as brine. The saturation index of minerals is calculated using models of Debye and Hückel and Harvie-Møller-Weare (Bethke, 2002). The TOUGHREACT uses (EOS) to calculate the mass balance. The (EOS) performs two important functions: i) calculates the volume fraction of each mineral at the time of water-rock interaction; and ii) uses the dissolution/precipitation of minerals identifying the change of each mineral phase.

The simulations results show some differences, because each software uses different numerical methods to solve a different set of reactions. When the user makes a choice of the software for geochemical modeling, it should be considered the differences of each code. In this way the user can reproduce the reactions of the geological environment of interest with greater approximation of reality. At high temperatures (120°C) there is an increasing convergence of the results among the different codes used in this study, due to the higher kinetic energy involved in geochemical reactions and the changes of thermodynamic parameters on temperature coefficients favor the precipitation/dissolution.

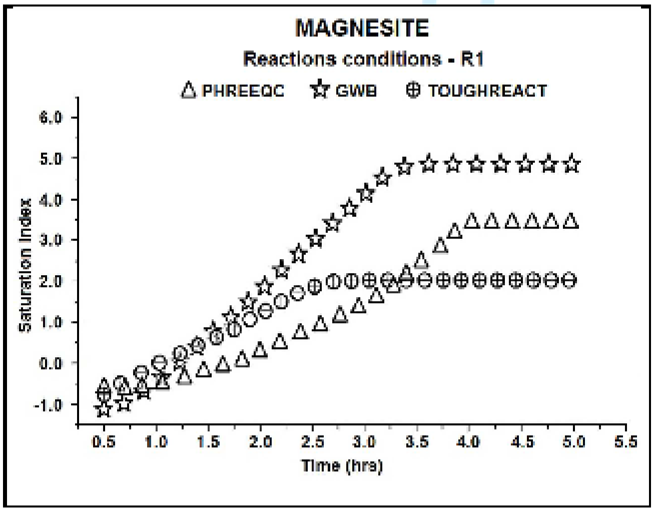


Fig. 9. Saturation index of magnesite in in reaction condition R1

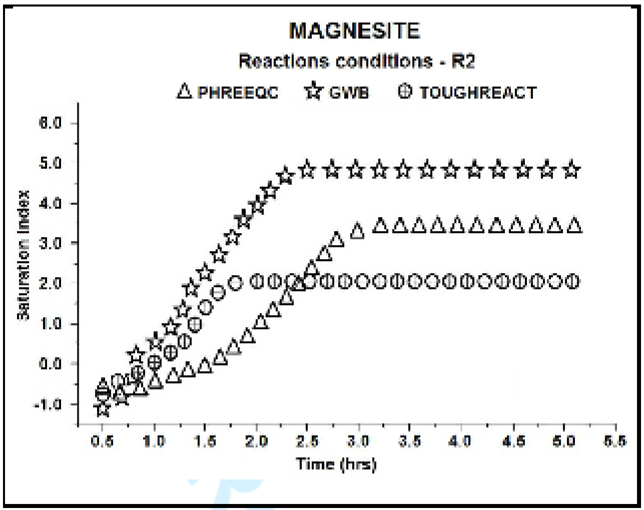


Fig. 10. Saturation index of magnesite in in reaction condition R2

3.5. Geochemical speciation of Mg-carbonate system and Mg-evaporite system

The general concept of speciation applies to many chemical systems. It is mostly common used in the context of aqueous solutions (Graeme et al. 2009). Typically, such solutions include natural water systems, such as sea, river, ground and lake waters. Natural waters can be considered as multi-component solutions where a network of interactions is established leading to the formation of chemical species with different thermodynamic stability. The different chemical behavior of ions in the medium leads to a different quantitative distribution of species depending on the kinetics of process. The term chemical speciation is generally used to assess the distribution of a certain chemical species under different chemical forms and oxidation states (Gianguzza et al. 1999; Gianguzza et al. 2000). Therefore various reactions and processes (complexation, oxidation/reduction, precipitation/dissolution) depending on both the reactivity of the chemical species and environmental conditions of the medium (temperature, pH, pe, oxidation, surface properties) where reactions and processes occur (Gianguzza et al. 2004). A numerical simulation study, predict the geochemical speciation of Mg-carbonate system (table 2) was carried out with GWB software.

Although the numerical modeling provides a variety of species present in evaporite-CO_2 interaction, we find some discrepancies when compared with the analyzes analysis carried out in the precipitate after the experiments. According to the geochemical modeling, some phases formed in Mg-carbonate system are hydromagnesite, nesquehonite, artinite, brucite and magnesite (Table 2). These carbonate minerals are present in the carbonation reactions using CO_2 partial pressures. Therefore, chloromagnesite, MgOHCl, $MgCl_2.H_2O$, $MgCl_2.2H_2O$,

$MgCl_2.4H_2O$, $Mg_2Cl(OH)_3.4H_2O$ and bischofite, which are present in our geochemical modelling, form a system of evaporitic rocks (Table 2).

Table 2
List of selected minerals in the Mg-carbonate system at 25°C as reported in the database of GWB.

Mineral species	Dissociation reaction
Artinite	$MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O + 3H^+ \leftrightarrow 2Mg^{2+} + HCO_3^- + 5H_2O$
Brucite	$Mg(OH)_2 + 2H^+ \leftrightarrow Mg^{2+} + 2H_2O$
Bischofite	$MgCl_2 . 6H_2O \leftrightarrow Mg^{2+} + 2Cl^- + 6H_2O$
Chloromagnesite	$MgCl_2 \leftrightarrow Mg^{2+} + 2Cl^-$
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 . 4H_2O + 6H^+ \leftrightarrow 4HCO_3^- + 5Mg^{2+} + 6H_2O$
Magnesite	$MgCO_3 + H^+ \leftrightarrow HCO_3^- + Mg^{2+}$
Nesquehonite	$Mg(HCO_3)(OH) . 2H_2O + H^+ \leftrightarrow Mg^{2+} + HCO_3^- + 3H_2O$
MgOHCl	$MgOHCl + H^+ \leftrightarrow Mg^{2+} + Cl^- + H_2O$
$MgCl_2 . H_2O$	$MgCl_2 . H_2O \leftrightarrow Mg^{2+} + 2Cl^- + H_2O$
$MgCl_2 . 2H_2O$	$MgCl_2 . 2H_2O \leftrightarrow Mg^{2+} + 2Cl^- + 2H_2O$
$MgCl_2 . 4H_2O$	$MgCl_2 . 4H_2O \leftrightarrow Mg^{2+} + 2Cl^- + 4H_2O$
$Mg_2Cl(OH)_3 . 4H_2O$	$Mg_2Cl(OH)_3 . 4H_2O + 3H^+ \leftrightarrow 2Mg^{2+} + Cl^- + 7H_2O$

There are large discrepancies for the product solubility and free energy of magnesite ($MgCO_3$) formation. Reviews of existing data (e.g.,Langmuir, 1965; Christ and Hostetler, 1970; Kittrick and Peryea, 1986; Könisberger et al., 1999; Marion, 2001) showed that reported values of the solubility product at room temperature ranged from $10^{-10.3}$ to $10^{-5.1}$, and free energy ($\Delta_f G^0_{298.15}$) of formation ranged from −1012.1 (kJ mol^{-1}) to −1030.709 (kJ mol^{-1}) (Wagman et al. 1982; Chernosky and Berman 1989).

This variation of magnesite solubility product has consequences on the relative stability of the various mineral phases of the Mg-carbonate. Langmuir (1965) explained the general scarcity of Mg-carbonates in natural environments by their high solubilities and assigned to magnesite a solubility product of $10^{-5.1}$, higher than that of nesquehonite ($MgCO_3{\cdot}3H_2O$, $Ksp=10^{-5.0}$) and hydromagnesite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$, $Ksp=10^{-4.9}$). However, according to more recent determinations of solubility and Gibbs free energy of formation (Kittrick and Peryea, 1986; Könisberger et al., 1999), magnesite appears to be the most stable carbonate phase forming in the system Mg-carbonate, under all conditions of temperature and CO_2 partial pressure, as also reported by Marion (2001) and Hänchen et al. (2008).

All other hydrated Mg-carbonates are unstable with respect to magnesite but their formation is favored by the slow kinetics of crystallization of magnesite, commonly attributed to the strongly hydrated character of the Mg^{2+} ion (Lippmann, 1973; Sayles and Fyfe, 1973). Nesquehonite precipitates at 25°C under moderate CO_2 pressures from solutions that are also supersaturated with respect to hydromagnesite and magnesite (Dell and Weller, 1959; Davies and Bubela, 1973; Hänchen et al., 2008). Nesquehonite successively transforms into hydromagnesite, with appearance of dypingite ($4MgCO_3Mg(OH)_2{\cdot}5H_2O$) as transitory phase, but an increase of temperature to about 50°C is required to make this process fast (Davies and Bubela, 1973; Hopkinson et al., 2008). Artinite ($MgCO_3{\cdot}Mg\ (OH)_2{\cdot}3H_2O$) is found at relatively lower pCO_2 conditions with respect to nesquehonite but its field of stability is limited by the presence of the other hydrous phases (Könisberger et al., 1999).

In summary, within the system considered here, only the phase transition brucite↔magnesite defines a stable equilibrium (see Könisberger et al., 1999), with magnesite being more stable at relatively high CO_2 partial pressures. The stability order among Mg-carbonate phases can be thus schematized as follows (Marion, 2001): magnesite→ hydromagnesite → nesquehonite.

Recently, interest on the Mg-carbonate formation has aroused because of the potential to use Mg-carbonate to fix carbon dioxide (CO_2) into stable and environmentally benign solids, employing Carbon Capture systems such as mineral carbonation and underground storage in sandstone, evaporite, mafic and ultramafic rock formations (IPCC 2005; Morad et al., 1994; Purvis 1992; Wilkinson et al., 2009; Drijkoningen et al., 2011). Magnesium-rich minerals are promising raw material for carbon dioxide (CO_2) sequestration because of their sufficient stability. It has been reported that Qaidam Basin, located in the northwest of China, stores more than 2 billion tons of bischofite ($MgCl_2{\cdot}6H_2O$), which theoretically can sequester more than 800 million tons of CO_2. Furthermore, bischofite is a byproduct of sea water desalinization, which could also be utilized by areas close to shoreline for CO_2 sequestration purpose (Yao et al. 2015). Precipitation of magnesium carbonate from the H_2O–CO_2–Na_2CO_3–$MgCl_2$ system was investigated by Hänchen M. et al 2008. The formation of the anhydrous form of magnesium carbonate, i.e., magnesite, has been demonstrated at 120°C and a PCO_2 of 3 bar.

4. Conclusion

The reactions between Mg^{2+} ions and $CO_{2(g)}$ performed in our experiments promoted Mg-carbonate precipitation with high purity of magnesite. The stabilization of the Mg-carbonate is strongly dependent on final pH of the solution, which is determined by the dissolved amount of the carbonated species.

The study of geochemical modeling with TOUGHREACT, GWB and PRHEEQC models: i) suggest the formation of magnesite; ii) converge in results for temperatures around 120°C, in which there is high kinetic energy and consequently the reactions take place with higher intensity; and iii) suggest that the mathematical interpolations in high temperatures are more numerically stable and accurate, causing convergence of the results. In this way, each simulator seeks each own best set of numerical solutions to achieve the equilibrium. In order to build a geological model, the user needs to be cautious in choosing geochemical modeling software, as an important factor for choosing a simulator is to know the temperature range that will be used.

The most important point of the Mg-carbonates system is to use Mg as CO_2 capture. The CO_2 would then be compressed and transported for storage in geological formations, in the ocean, in mineral carbonates, or for use in industrial processes, fixation of CO_2 into inorganic carbonates. From a thermodynamic viewpoint, inorganic carbonates represent a lower energy state than CO_2; hence the carbonation reaction is exothermic and can theoretically yield energy. However, the kinetics of natural mineral carbonation is slow; hence all currently implemented processes require energy intensive preparation of the solid reactants to achieve affordable conversion rates and/or additives that must be regenerated and recycled using external energy sources. The resulting carbonated solids must be stored at an environmentally suitable location. The technology is still in the development stage and is not yet ready for implementation large-scale.

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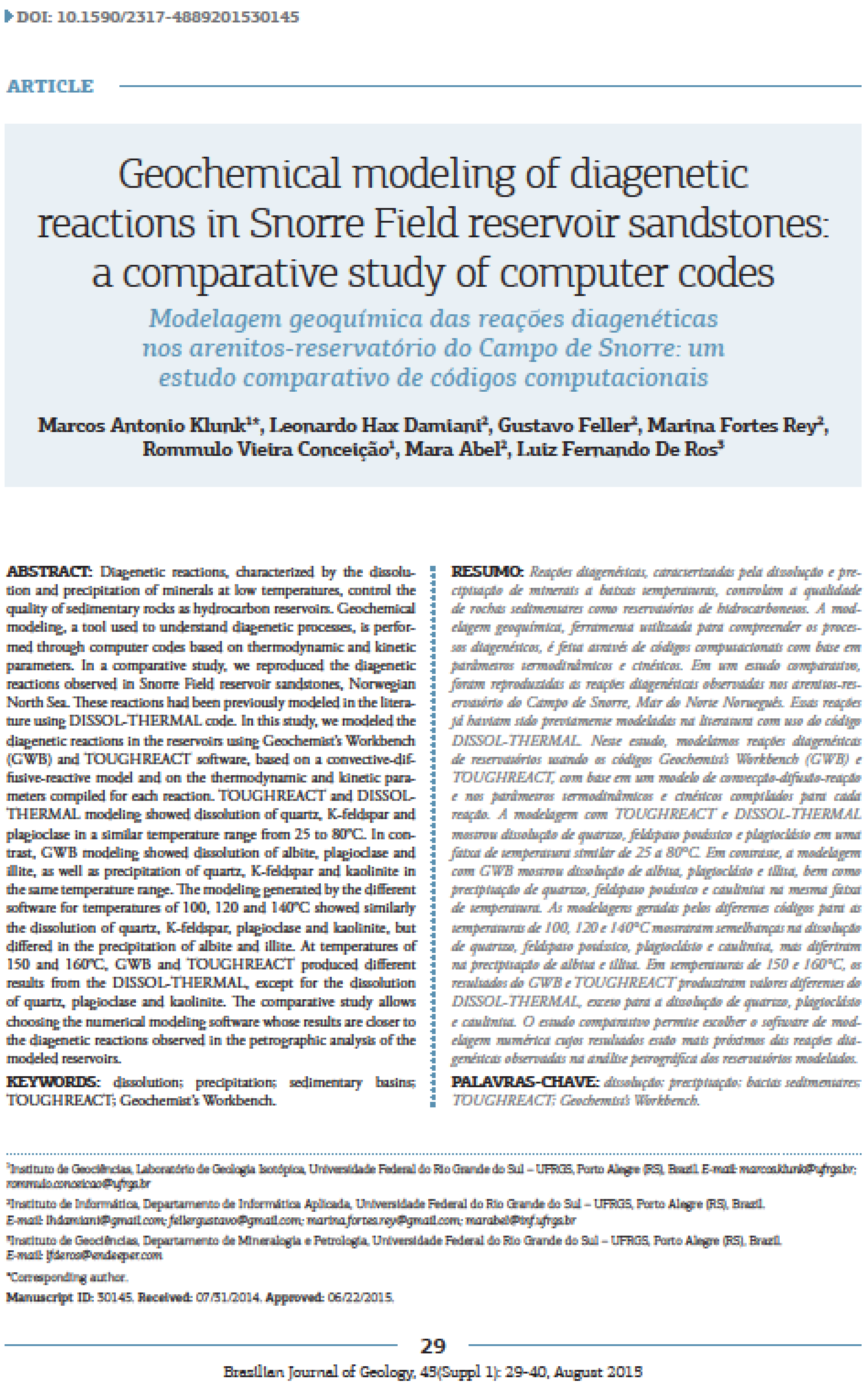

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ARTICLE

Geochemical modeling of diagenetic reactions in Snorre Field reservoir sandstones: a comparative study of computer codes

Modelagem geoquímica das reações diagenéticas nos arenitos-reservatório do Campo de Snorre: um estudo comparativo de códigos computacionais

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ABSTRACT: Diagenetic reactions, characterized by the dissolution and precipitation of minerals at low temperatures, control the quality of sedimentary rocks as hydrocarbon reservoirs. Geochemical modeling, a tool used to understand diagenetic processes, is performed through computer codes based on thermodynamic and kinetic parameters. In a comparative study, we reproduced the diagenetic reactions observed in Snorre Field reservoir sandstones, Norwegian North Sea. These reactions had been previously modeled in the literature using DISSOL-THERMAL code. In this study, we modeled the diagenetic reactions in the reservoirs using Geochemist's Workbench (GWB) and TOUGHREACT software, based on a convective-diffusive-reactive model and on the thermodynamic and kinetic parameters compiled for each reaction. TOUGHREACT and DISSOL-THERMAL modeling showed dissolution of quartz, K-feldspar and plagioclase in a similar temperature range from 25 to 80°C. In contrast, GWB modeling showed dissolution of albite, plagioclase and illite, as well as precipitation of quartz, K-feldspar and kaolinite in the same temperature range. The modeling generated by the different software for temperatures of 100, 120 and 140°C showed similarly the dissolution of quartz, K-feldspar, plagioclase and kaolinite, but differed in the precipitation of albite and illite. At temperatures of 150 and 160°C, GWB and TOUGHREACT produced different results from the DISSOL-THERMAL, except for the dissolution of quartz, plagioclase and kaolinite. The comparative study allows choosing the numerical modeling software whose results are closer to the diagenetic reactions observed in the petrographic analysis of the modeled reservoirs.

KEYWORDS: dissolution; precipitation; sedimentary basins; TOUGHREACT; Geochemist's Workbench.

RESUMO: *Reações diagenéticas, caracterizadas pela dissolução e precipitação de minerais a baixas temperaturas, controlam a qualidade de rochas sedimentares como reservatórios de hidrocarbonetos. A modelagem geoquímica, ferramenta utilizada para compreender os processos diagenéticos, é feita através de códigos computacionais com base em parâmetros termodinâmicos e cinéticos. Em um estudo comparativo, foram reproduzidas as reações diagenéticas observadas nos arenitos-reservatório do Campo de Snorre, Mar do Norte Norueguês. Essas reações já haviam sido previamente modeladas na literatura com uso do código DISSOL-THERMAL. Neste estudo, modelamos reações diagenéticas de reservatórios usando os códigos Geochemist's Workbench (GWB) e TOUGHREACT, com base em um modelo de convecção-difusão-reação e nos parâmetros termodinâmicos e cinéticos compilados para cada reação. A modelagem com TOUGHREACT e DISSOL-THERMAL mostrou dissolução de quartzo, feldspato potássico e plagioclásio em uma faixa de temperatura similar de 25 a 80°C. Em contraste, a modelagem com GWB mostrou dissolução de albita, plagioclásio e illita, bem como precipitação de quartzo, feldspato potássico e caulinita na mesma faixa de temperatura. As modelagens geradas pelos diferentes códigos para as temperaturas de 100, 120 e 140°C mostraram semelhanças na dissolução de quartzo, feldspato potássico, plagioclásio e caulinita, mas diferiram na precipitação de albita e illita. Em temperaturas de 150 e 160°C, os resultados do GWB e TOUGHREACT produziram valores diferentes do DISSOL-THERMAL, exceto para a dissolução de quartzo, plagioclásio e caulinita. O estudo comparativo permite escolher o software de modelagem numérica cujos resultados estão mais próximos das reações diagenéticas observadas na análise petrográfica dos reservatórios modelados.*

PALAVRAS-CHAVE: *dissolução; precipitação; bacias sedimentares; TOUGHREACT; Geochemist's Workbench.*

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INTRODUCTION

Petroleum systems are dynamic physical-chemical environments of generation, migration and storage of oil. Initially, oil is generated in a rock rich in organic matter that suffers a maturation process in specific depth and temperature (source rock). The oil then migrates to a porous lithology that will store it (the reservoir rock), where it is trapped by another rock that has low permeability (the seal) (Magoon & Dow 1994; Gluyas & Swarbrick 2004).

Unlike the seal rocks, reservoir rocks are characterized by high porosity and permeability. The reservoirs are normally carbonate rocks (Roehl & Choquette 1985) or siliciclastic rocks (Barwis *et al.* 1990), formed as the result of several transformations that occur in the deposited sediments, via modification of the original texture, composition and, consequently, in the porosity. Such processes are called diagenesis.

The most common diagenetic processes that affect the porosity and permeability of reservoirs are compaction and precipitation of various types of carbonates, silicates and other minerals (Tucker 2001). If precipitated as cements in significant amounts in the space between the primary depositional constituents, these diagenetic minerals compromise the porosity of the rocks, making them unfeasible as a reservoir. Nevertheless, there is also the possibility of subsequent dissolution of diagenetic cements, generating secondary porosity, as occurs in many reservoirs (Bjorlykke 1984; Schmidt & McDonald 1979; Surdam *et al.* 1984).

The diagenetic processes allow a variety of minerals to occur as cement in sedimentary rocks. The most common cements are:

1. quartz in the form of secondary overgrowths around detrital grains and intergranular microcrystals;
2. K-feldspar as secondary overgrowths or discrete crystals filling pores;
3. carbonates, like calcite and dolomite, siderite and more rarely ankerite, rhodochrosite and magnesite;
4. clay minerals, like kaolinite, illite, chlorite, smectite and interstratified mixed-layers (especially illite-smectite).

Clay minerals are volumetrically less significant, but extremely important, since they commonly occur as rims or coatings around grains, exerting enormous influence on the permeability of rocks, damaging the quality of reservoirs (Houseknecht & Pittman 1992).

Chemical phenomena are the most common during diagenesis, comprising reactions that result in precipitation of authigenic minerals or secondary dissolution. From the geochemical point of view, these reactions occur because the constituents of the sediments are always trying to reach equilibrium, and, therefore, tend to interact with the interstitial fluids through diagenetic processes (Burley *et al.* 1985). The diagenetic processes are controlled not only by temperature (T), pressure (P) and the original mineral assemblage, but also by the activities of the ions dissolved in the formation waters, including organic solutes, Eh and pH conditions.

Galloway (1984) establishes three main hydrological regimes for fluids within sedimentary basins, related to their movement and occurrence:

1. meteoric regime, affecting the shallower portions of basins, characterized by infiltration of surface to groundwaters;
2. compactional regime, linked to expulsion of pore waters due to burial;
3. thermobaric or abyssal regime, associated to the deeper parts of the basins, where the interstitial fluids are affected by clay minerals dehydration and oil generation.

Geochemical modeling is a tool used to understand the diagenetic processes. It is performed through computer codes based on thermodynamic and kinetic parameters. However, since there are several mutually-influencing parameters, each code must be used carefully in order to better simulate the natural conditions. In this study, we reproduced the diagenetic reactions observed in the Snorre Field sandstones reservoir, Norwegian North Sea using Geochemist's Workbench (GWB) and TOUGHREACT software, based on a convective-diffusive-reactive model, and the thermodynamic and kinetic parameters compiled for each reaction. The Snorre Field was chosen considering the availability of petrographic and stratigraphic data to build a conceptual model of the diagenetic reactions (Baccar & Fritz 1993; Morad *et al.* 1990). Nevertheless, such study has potential application to the modeling of Brazilian reservoirs with similar composition, depositional and burial evolution.

Baccar and Fritz (1993) modeled the diagenetic reactions in Snorre Field reservoir sandstones using DISSOL-THERMAL code. We reproduced the same study using GWB and THOUGHREACT codes, so that we could evaluate similarities and divergences in the results of each system according to a wide temperature range.

GEOCHEMICAL MODELING APPROACH

Although the fundamental concepts of chemical modeling have evolved much before, geochemical modeling begins in the 1960s, with the pioneering efforts of researchers such as Garrels and Mackenzie (1967), Helgeson (1967a, 1967b), and Helgeson and James (1968). The first simulations were originally applied to the understanding of the basic issues involving chemical reactions in aquatic environments related to pollution of surface waters and assessment of diagenetic processes (involving natural formation and alteration of rocks).

A geochemical model is really only useful as a tool for prediction if there is the possibility to validate the results. In reality, this is the goal that most often is unattainable, due to the complexity of natural systems, insufficient field data and uncertainties related to changes in the system over time (Nordstrom 1994).

In the following sections, the main characteristics of TOUGHREACT and GWB, software used in this study, are described. We also give some characteristics of the DISSOL-THERMAL code used by Baccar and Fritz (1993).

TOUGHREACT

TOUGHREACT was developed to simulate fluid flow non-isothermal multi-component and geochemical transport, in order to investigate problems involving simple and complex geological environments (Xu & Pruess 1998). TOUGHREACT can also use "batch models", simulating the reactions in a closed system. A number of thermo-physical and chemical processes, which occur in the subsurface, are considered under the aspect of hydrological and geochemical conditions of pressure, temperature, water saturation and ionic strength. The code uses non-isothermal equations (Pruess 1987; Pruess *et al.* 1999). The numerical solution to the water-rock interaction is based on finite difference (Narasimhan & Witherspoon 1976). These equations are solved by the Newton-Raphson interaction (Pruess 1991). The activity coefficient is calculated using the Debye-Huckel equation (Helgeson *et al.* 1981).

Kinetic rates (mineral dissolution/precipitation) can be expressed as function of non-basis species as well. Usually the species appearing in rate laws happen to be basis species. In this model, we use a rate expression given by Lasaga *et al.* (1994):

$$r_n = A_n . k_n . (1 - \frac{Q}{K}) \tag{1}$$

where positive values of r_n indicate dissolution, and negative values indicate precipitation; k_n is the rate constant (moles per mineral surface area unit and time unit), which is temperature dependent; A_n is the specific reactive surface area per kg; and Q/K is the kinetic mineral saturation ratio. The temperature dependence of the reaction rate constant can be expressed reasonably well via an Arrhenius equation (Lasaga 1984; Steefel and Lasaga 1994). Because many rate constants are reported at 25°C, it is convenient to approximate rate constant dependency as a function of temperature, thus:

$$k_n = k_{25} . e^{\left[\frac{-Ea}{R}(\frac{1}{T} - \frac{1}{298.15})\right]} \tag{2}$$

where *e* is Euler's number; Ea is the activation energy; k_{25} is the reaction rate at 25°C; R is gas constant; and T is absolute temperature.

The kinetic rate constant k_n in equations 1 and 2 only considers the most well-studied mechanisms in pure H_2O (at neutral pH). Dissolution and precipitation of minerals are often catalyzed by H^+ (acid mechanism) and OH^- (base mechanism). For many minerals, the kinetic rate constant k includes each of these three mechanisms (Lasaga *et al.* 1994; Palandri & Kharaka 2004).

Geochemist's Workbench

The GWB system was developed by the Department of Geology at the University of Illinois at Urbana-Champaign in 1978. It is currently marketed by "Aqueous Solutions LLC" (http://www.gwb.com/). The software allows fast assessment of the problems most commonly encountered in geochemical modeling: balance reactions speciation in aqueous solution, water-rock interaction models, and fluid mixture in conditions of "batch model" (Bethke 2008).

GWB can integrate thermodynamic and kinetic parameters with species processing of geochemical reactions in redox environments (Drever 1997). The batch modeling is a process by which a series of irreversible reactions (no equilibrium) progress to a state of thermodynamic equilibrium (Helgeson *et al.* 1969). These reactions lead to chemical evolution of a system to reach the equilibrium state. To solve the equilibrium of an initial system, GWB determines which reactions are more likely to happen.

GWB solves simultaneously a set of non-linear algebraic equations, composed by the equation of mass action and the equilibrium constant, corresponding to aqueous species, gas or minerals that are contained in a database. While GWB solves the equation of mass action, it is solving all the mass balance of the system. The GWB solves the equations using Newton-Raphson method.

The GWB allows the user to build the rate law for the reactions kinetics. Settings are available for kinetic dissolution/precipitation reactions, redox reactions and microbial metabolism. The pattern that GWB uses for the equation of the rate law for the dissolution and precipitation of minerals takes the following form:

$$r_n = A_s . k + . (1 - \frac{Q}{K}) \tag{3}$$

where r_k is reaction rate; A_s is mineral surface area; k_+ is rate constant; Q is activity product; and K is equilibrium constant. The ratio Q/K is known as mineral saturation index.

In many cases, changes in the temperature will affect the rates of reactions in progress. In GWB, the activation energy and pre-exponential factor can be used to specify a temperature-dependent rate, based on the formulation of Arrhenius:

$$k+ = A \, . \, e^{\left[\frac{-Ea}{RT}\right]} \tag{4}$$

where A is pre-exponential factor; Ea is activation energy; R is gas constant; and T is absolute temperature.

Diagenesis is defined as the sum of physical and chemical changes during progressive burial and heating, reflected in compaction owing to known physical processes and to reactions where minerals are dissolved or precipitated. A wide variety of diagenetic reactions occur in sandstones, and some have significant effects on porosity and permeability.

Mathematical correlations between TOUGHREACT and Geochemist's Workbench, and kinetic parameters

The mathematical correlations of TOUGHREACT resemble in part those of GWB, but there is an important difference between them. Solving equation 2, we have:

$$k_n = k_{25} \, . \, e^{\left[\frac{-Ea}{RT} - \frac{Ea}{R298.15}\right]} \tag{5}$$

$$k_n = k_{25} \, . \, e^{\left[\frac{-Ea}{RT}\right]} . \, e^{\left[\frac{Ea}{R298.15}\right]} \tag{6}$$

Thus, the correlation of GWB with TOUGHREACT is:

$$k_{+} \, . \, A \, . \, e^{\left[\frac{-Ea}{RT}\right]} = k_{25} \, . \, e^{\left[\frac{-Ea}{RT}\right]} . \, e^{\left[\frac{Ea}{R298.15}\right]} \tag{7}$$

The major difference observed in TOUGHREACT is the numerical expression:

$$k_{25} \, . \, e^{\left[\frac{Ea}{R298.15}\right]} \tag{8}$$

The kinetic parameters used in the simulations are shown in Tab. 1. Each software has different numerical methods to solve the diagenetic reactions observed in the geological environment. Thus, the kinetic parameters adopted by each simulator are submitted to some adjustment factors.

After the kinetic parameters are inserted in each software interface, simulators calculate the "global rate constant", whose values are in Tab. 2.

If we look at two different reference books on the equilibrium constant value of a chemical reaction, there is a big chance that the values found are different (sometimes by a factor of 10 or more). This discrepancy is because the constant value may have been determined in different conditions and perhaps using different techniques. A common source of variation in published values of K is the ionic composition of the solution (Harris 2012).

The diagenetic reactions used by GWB and TOUGHREACT are shown in Tab. 3. For GWB, the equations are written with a view to all possible chemical equilibria, as a function of hydrogen ion. The GWB uses hydrogen ions (H^+) to assist in the dissociation of minerals, thus enabling the adjustment of the stoichiometric coefficients.

DISSOL-THERMAL

The DISSOL-THERMAL simulator (Fritz 1975, 1981) is a geochemical code able to predict whether the mineral constituents are dissolved or precipitated, as well as the composition of the solution after the water-rock interaction. Through the attributed concentration of dissolved species, temperature, pH, and redox potential, DISSOL-THERMAL code provides the diagenetic reactions and calculates the saturation index of minerals present in the geological environment.

DISSOL-THERMAL is divided into two geochemical codes:

1. DISSOL — calculates a model for simulating water-rock interactions at a given temperature between 0° and 300°C; and
2. THERMAL — calculates a model for simulating the effect of temperature variation on water-rock equilibrium.

These two codes both operate by combining an initial solution saturation test, followed by path calculation (dissolution or temperature variation).

In this study, we used the DISSOL-THERMAL modeling results from Baccar and Fritz (1993) and compared to our modeling using GWB and TOUGHREACT simulations.

INITIAL CONDITIONS OF THE RESERVOIR AND THE SIMULATION

Geological setting and mineralogy of Snorre Field reservoirs

The Snorre Field is located in the northern part of the North Sea (Fig. 1). The oil field is situated on the Tampen

Spur, which is a platform high on the western side of the Viking Graben (Jurassic-Cretaceous). The main reservoir horizons are fluvial sandstones from the upper member of the Upper Triassic Lunde Formation and the Upper Triassic to Lower Jurassic Statfjord Formation (Hollander 1987).

The Lunde Formation, which is the subject of this paper, is the uppermost formation of the Triassic Hegre Group (Vollset & Dore 1984). It was deposited during the thermal subsidence phase following a Late Permian to Earliest Triassic rifting episode (Badley *et al.* 1988; Nystuen *et al.* 1989). The Triassic to Middle Jurassic sequence on the Snorre Field was uplifted, tilted and partly eroded during the Kimmeridgian rifting episode in Late Jurassic to Early Cretaceous times. The uplift was followed by subsidence and burial during crustal cooling from Early Cretaceous to Recent (Morad *et al.* 1990).

The sandstones are dominantly fine- to medium-grained and arkosic, having as main framework constituents quartz, K-feldspar, plagioclase, muscovite, biotite and clay minerals, and as accessory constituents garnet, zircon, rutile, tourmaline, staurolite, sillimanite, kyanite and apatite.

Subordinate constituents include extrabasinal quartz-feldspar-mica rock fragments that probably represent granitic rocks and/or schists or gneisses. They also include mud and carbonate intraclasts. Micas and detrital clay minerals seldom make up more than 2% of the total mineral content in the sandstones. Clay minerals of detrital origin include smectite, mixed-layer clay minerals, chlorite and subordinate amounts of kaolinite and illite.

Diagenetic clay minerals include pore-filling kaolinite and pore-lining smectite, mixed-layer chlorite-smectite, and

Table 1. Kinetics parameters used in each software (Palandri & Kharaka 2004).

Minerals	GWB	TOUGHREACT
Quartz	Pre-exponential factor: 0.033 mol/cm^2/s	Pre-exponential factor: 4.11e-06 mol/m^2/s
	Activation energy: 90900 J/mol	Activation energy: 90.90 kJ/mol
	Grain size: not used	Grain size: 0.001 mm
	Surface area: 17.5 cm^2/g	Surface area: 17.5 cm^2/g
Albite	Pre-exponential factor: 2.75e-09 mol/cm^2/s	Pre-exponential factor: 2.75e-13 mol/m^2/s
	Activation energy: 69800 J/mol	Activation energy: 69.80 kJ/mol
	Grain size: not used	Grain size: 0.001 mm
	Surface area: 8.0 cm^2/g	Surface area: 8.0 cm^2/g
K-feldspar	Pre-exponential factor: 3.89e-09 mol/cm^2/s	Pre-exponential factor: 3.89e-13 mol/m^2/s
	Activation energy: 38000 J/mol	Activation energy: 38.00 kJ/mol
	Grain size: not used	Grain size: 0.001 mm
	Surface area: 16.0 cm^2/g	Surface area: 16.0 cm^2/g
Anorthite	Pre-exponential factor: 7.58e-6 mol/cm^2/s	Pre-exponential factor: 7.58e-10 mol/m^2/s
	Activation energy: 17800 J/mol	Activation energy: 17.8 kJ/mol
	Grain size: not used	Grain size: 0.001 mm
	Surface area: 2.0 cm^2/g	Surface area: 2.0 cm^2/g
Illite	Pre-exponential factor: 1.08e-12 mol/cm^2/s	Pre-exponential factor: 1.08e-16 mol/m^2/s
	Activation energy: 30430 J/mol	Activation energy: 30.43 kJ/mol
	Grain size: not used	Grain size: 0.0005 mm
	Surface area: 8.0 cm^2/g	Surface area: 8.0 cm^2/g
Kaolinite	Pre-exponential factor: 6.60e-10 mol/cm^2/s	Pre-exponential factor: 6.60e-14 mol/m^2/s
	Activation energy: 22200 J/mol	Activation energy: 22.20 kJ/mol
	Grain size: not used	Grain size: 0.0001 mm
	Surface area: 16.0 cm^2/g	Surface area: 16.0 cm^2/g

chlorite. Diagenetic kaolinite also replaces detrital micas and feldspars. Other cements include carbonates, which play a significant role in porosity reduction in some of the sandstones. The most dominant are calcite and ferroan-calcite. Dolomite and ankerite, however, are also present in many of the samples, especially above the oil-water contact, and within 100 m of the Kimmeridgian unconformity (Fig. 2).

Calcite occurs mainly as nodular to patchy pore-filling or replacive poikilotopic cement. Replacement of calcite by ferroan-dolomite was observed by Morad *et al.* (1990). Ferroan-dolomite and ankerite are commonly associated with detrital biotite. Siderite is a subordinate cement in these sandstones, but does occur in the flood plain sediments, predominantly as nodules. Authigenic quartz overgrowths (< 1%) are rarely observed. Authigenic bipyramidal crystals of anatase (< 1%) are recorded in most of the studied samples. Other minor authigenic cements include albite overgrowths, pyrite and barite (Morad *et al.* 1990).

The diagenetic evolution of the upper member of the Lunde Formation has been controlled by water-rock reactions acting during deposition, burial through the cooling phase succeeding the Permo-Triassic rifting episode, Kimmeridgian rifting and uplift, and post- Kimmeridgian burial. Over this time interval, four major diagenetic regimes (*cf.* Schmidt & McDonald 1979) are recognized:

1. Eodiagenesis in the late Triassic;
2. Mesodiagenesis in the late early Jurassic to late Jurassic;
3. Telodiagenesis in the latest Jurassic through early Cretaceous; and

Table 2. Rate constant and equilibrium constant used by each software.

Mineral	GWB		TOUGHREACT	
	Equilibrium constant (log K)	Rate constant (mol/cm^2/s)	Equilibrium constant (log K)	Rate constant (mol/cm^2/s)
Quartz	-3.99	7.12e-18	-3.74	7.00e-18
Albite	-18.02	2.55e-21	-19.13	4.32e-21
K-feldspar	-20.57	1.09e-15	-21.91	4.97e-15
Anorthite	-19.71	6.47e-09	-19.19	8.50e-10
Illite	-40.26	6.13e-18	-42.33	1.31e-17
Kaolinite	7.43	9.83e-14	6.81	7.62e-14

GWB: Geochemist's Workbench.

Table 3. Dissociation reaction of the minerals according to the software.

Minerals	Dissociation reaction
Quartz (SiO_2)	*Quartz $\leftrightarrow 1SiO_{2(aq)}$
	**Quartz $\leftrightarrow 1SiO_{2(aq)}$
Albite ($NaAlSi_3O_8$)	*Albite $+ 4H^+ \leftrightarrow Na^+ + Al^{+3} + 3SiO_{2(aq)} + 2H_2O$
	**Albite $\leftrightarrow Na^+ + AlO_2^- + 3SiO_{2(aq)}$
K-feldspar ($KAlSi_3O_8$)	*K-feldspar $+ 4H^+ \leftrightarrow 1K^+ + Al^{+3} + 3SiO_{2(aq)} + 2H_2O$
	**K-feldspar $\leftrightarrow 1K^+ + AlO_2^- + 3SiO_{2(aq)}$
Anorthite ($CaAl_2(SiO_4)_2$)	*Anorthite $+ 8H^+ \leftrightarrow 1Ca^{+2} + 2Al^{+3} + 2SiO_2 + 4H_2O$
	**Anorthite $\leftrightarrow 1Ca^{+2} + 2AlO_2^- + 2SiO_{2(aq)}$
Illite ($K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$)	*Illite $+ 8H^+ \leftrightarrow 0.6K^+ + 0.25Mg^{+2} + 2.3Al^{+3} + 3.5SiO_{2(aq)} + 5H_2O$
	**Illite $\leftrightarrow 0.6K^+ + 0.25Mg^{+2} + 2.3AlO_2^- + 3.5SiO_{2(aq)} + 4H_2O + 1.2H^+$
Kaolinite ($Al_2Si_2O_5(OH)_4$)	*Kaolinite $+ 6H^+ \leftrightarrow 2Al^{+3} + 2SiO_{2(aq)} + 5H_2O$
	**Kaolinite $\leftrightarrow 2AlO_2^- + 2SiO_{2(aq)} + 1H_2O + 2H^+$

*Geochemist's Workbench; **TOUGHREACT.

4. Mesodiagenesis in the mid-Cretaceous to recent.

Geochemical modeling of diagenetic events

Baccar and Fritz (1993) studies were focused on the mesodiagenesis, in which there were several interactions between the rocks and modified waters in different temperatures. Our studies are referred to the same conditions. The scenario that will be modeled in this study is the interaction of Lunde Formation with a modified seawater in different conditions of temperature, which correspond to mesodiagenesis conditions (Morad *et al.* 1990).

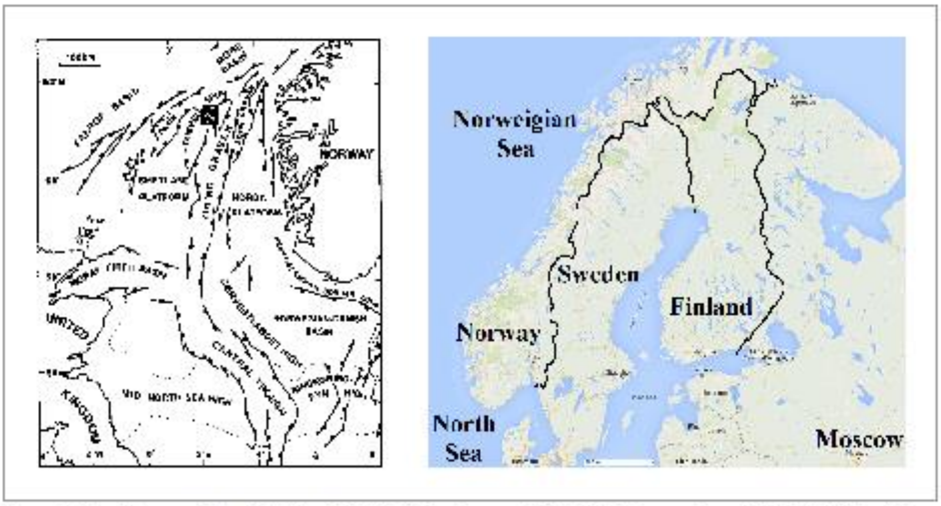
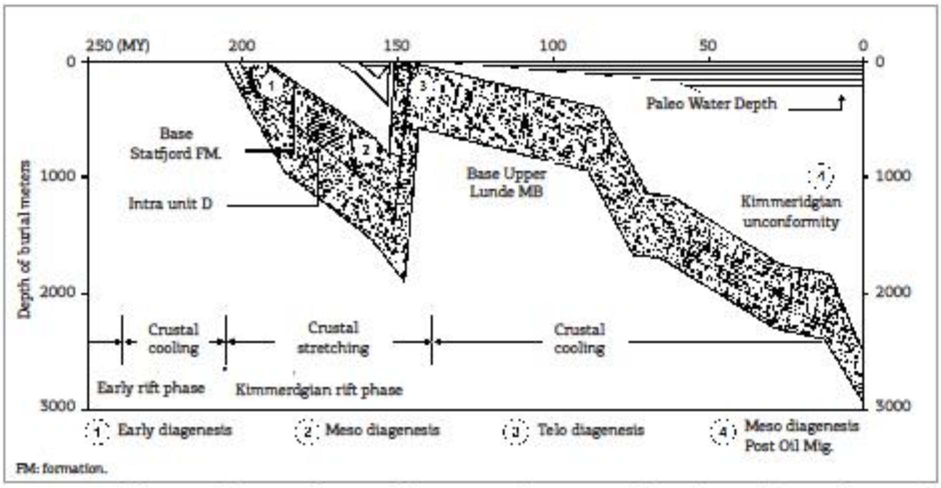


Figure 1. Location map (blocks 34/7 and 34/4) of the Snorre Field at the Tampen Spur in the North Sea (from Morad *et al.* 1990).



FM: formation.

Figure 2. Burial history and associated stages of diagenesis in the upper Lunde Member sandstones (from Morad *et al.* 1990).

The primary rock is a sandstone with an average simplified composition of 70% quartz, 20% feldspars and 10% clays. The complete mineral composition of this rock is detailed in Tab. 4 and the quantity of each mineral is represented by volume fraction dissolved per kg of H_2O. Seawater composition was compiled from Nordstrom *et al.* (1979), and the major element composition is shown in Tab. 5. Diagenetic events are modeled in the following temperatures:

- Event 1: 25, 40, 60 and 80°C;
- Event 2: 100, 120 and 140°C;
- Event 3: 150 and 160°C.

RESULTS

Diagenetic processes, as predicted by modeling the water-rock interaction between 25 and 160°C using TOUGHREAT and GWB, in comparison to DISSOL-THERMAL, are summarized in Fig. 3. The modeling with TOUGHREACT and DISSOL-THERMAL showed dissolution of quartz, K-feldspar, plagioclase, kaolinite and illite between 25 and 160°C. When GWB was used, quartz, K-feldspar, albite, illite and kaolinite were precipitated.

At temperatures of 100, 120 and 140°C, the 3 different modeling systems indicate the dissolution of quartz, K-feldspar, plagioclase and kaolinite, converging regarding their results.

At temperatures of 150 and 160°C, GWB and TOUGHREACT produce different results from those of DISSOL-THERMAL with dissolution of K-feldspar.

Above 100°C, we observed similar behavior in GWB and TOUGHREACT modeling due to the high kinetics and thermodynamics involved in diagenetic reactions, favoring the polynomial equations used by simulators.

DISCUSSION

As showed in the results, the use of different codes produces different results during modeling. The convergence of results is more evident between TOUGHREACT and DISSOL-THERMAL than between DISSOL-THERMAL and GWB software. Generally at low temperatures, the simulation results show some discrepancies, because each software uses different numerical methods to solve a different set of reactions.

The choice of the software for geochemical modeling should consider the differences of each code, in a way to reproduce the reactions of the geological environment of interest with greater approximation of reality.

At low temperatures ($T < 80°C$), it is not possible to observe similarity among the results of the different codes due to the low kinetic energy involved in the diagenetic reactions. Each simulator has its own algorithms based on mathematical codes that are dependent on kinetic and thermodynamic parameters of each mineral, contained in database.

In the physical-chemical approach to higher temperature reactions, the kinetic energy increases to the point to generate similar results, regardless of the model. In the present study, it is shown that at elevated temperatures (100 to 140°C) there is an increase in kinetic energy, incrementing the intensity of the diagenetic reactions.

Table 4. Mineralogical composition of the reacting rock (Lunde Sandstone, Triassic, North Sea) (Morad *et al.* 1990).

Minerals	Chemical formula	Volume fraction
Quartz	SiO_2	70.00
Albite	$NaAlSi_3O_8$	5.00
K-feldspar	$KAlSi_3O_8$	8.00
Anorthite	$CaAl_2Si_2O_8$	7.00
Illite	$Si_{3.49}Al_{2.34}Mg_{0.38}O_{10}(OH)_2K_{0.6}$	5.00
Kaolinite	$Si_2Al_2O_5(OH)_4$	5.00

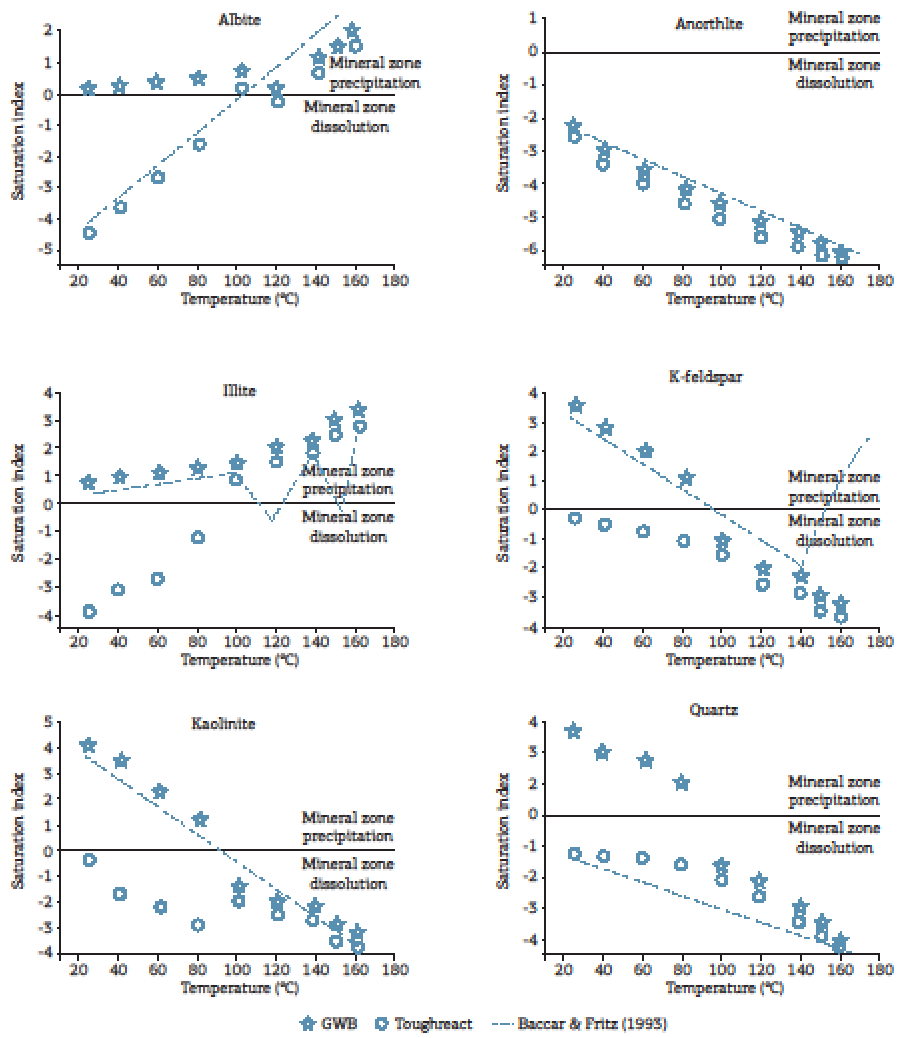
Table 5. Chemical composition of the initial solution (mM/L) — sea water, at 25°C (Nordstrom *et al.* 1979).

Al^{3+}	K^+	Na^+	Ca^{2+}	Mg^{2+}	Fe^{2+}	SiO_2	SO_4^{2-}	Cl^-	pH
7.59×10^{-8}	10.45	479.32	10.53	54.39	3.66×10^{-8}	0.073	28.893	559.5	8.22

Alkalinity = 2.376 meq/L; Eh = 500 mV.

Consequently, the GWB, TOUGHREACT and DISSOL-THERMAL systems generate similar results. However, GWB and THOUGHREACT have different approaches while working with high temperatures when compared to the DISSOL-THERMAL. This can be observed by the behavior of illite and K-feldspar.

In general, above 100°C, GWB and TOUGHREACT reproduce similar behavior. The numerical method of both systems uses



GWB: Geochemist's Workbench.

Figure 3. Geochemical modeling of a sandstone from North Sea using the Geochemist's Workbench and TOUGHREACT software, in comparison with the results obtained by Baccar and Fritz (1993).

polynomial equations of 8th grade to resolve the physical-chemical interactions in geological environments. These equations are dependent on kinetic and thermodynamic data of minerals that form parageneses in sandstone reservoirs. For temperatures above 140°C, these kinetic and thermodynamic data acquire an anomalous behavior for some minerals, indicated by the constant value of 500. If the software finds the 500 value, the previous value is used. This is just a reference approach to indicate that that value has not been calculated.

TOUGHREACT uses equations of state (EOS) to calculate the mass balance. The EOS perform two important functions:

1. to calculate the volume fraction of each mineral at the time of water-rock interaction;
2. to use the dissolution/precipitation of minerals identifying the change of each mineral phase.

From the variation in the minerals volume, it is possible to calculate the porosity and permeability.

The software that is most similar to DISSOL-THERMAL in the condition of this study is TOUGHREACT. This similarity is due to the mathematical treatment as discretization technique (method to solve the differential equations) and the finite difference method, providing flexibility in the description of the geometry of the reservoir. These numerical approximations increase the resolution of water-rock interaction.

Basically, this comparative study revealed two diagenetic stages, taking into account the temperature. The first stage corresponds to the temperature range of 25 – 100°C, and the second stage, to the temperature range of 120 – 160°C. In the lower temperature stage (25 – 100°C), TOUGHREACT and DISSOL-THERMAL simulators reproduce the diagenetic reactions among minerals albite, anorthite and quartz. However, GWB and DISSOL-THERMAL software assume a similarity of geochemical reactions among a larger number of minerals such as illite, kaolinite, K-feldspar and anorthite. In the higher temperature stage (120 – 160°C), we find a similar behavior in the 3 systems, due to the convergence of their numerical methods, as it is evident in Fig. 3.

Users must be careful when choosing a geochemical modeling software because, depending on the temperature range, different systems can produce very discrepant behaviors. Although GWB and DISSOL-THERMAL simulators reproduced the largest number of similar diagenetic reactions, users must be cautious in interpreting their data.

CONCLUSIONS

The present study of geochemical modeling comparing the application of GWB, TOUGHREACT and DISSOL-THERMAL codes for the simulation of diagenetic reactions observed in the Snorre Field reservoir sandstones, Norwegian North Sea, resulted in the following conclusions:

1. Diagenetic modeling at low temperatures (25 to 80°C) with different simulators reproduce quite different behaviors. In this temperature range, which involves low energy, the reaction kinetics and the thermodynamic parameters are treated according to the particularities of each code. The numerical methods used by GWB and TOUGHREACT software are able to achieve only limited convergence of results, with low precision expected for diagenetic reactions at low-temperature geological environments.
2. For the range of temperature from 100 to 140°C, in which there is higher kinetic energy involved and consequently the diagenetic reactions take place with higher intensity, the simulations with all the three systems generate similar results, because they use the same mass balance and the same temperature variation for the precipitation/dissolution of minerals. The mathematical interpolations used by simulators in this temperature range are more stable and numerically accurate, giving rise to a greater convergence of results.
3. For higher temperatures, from 150 to 160°C, GWB and TOUGHREACT reproduced the same behavior of dissolution/precipitation of minerals. However, when compared to DISSOL-THERMAL code, those results are discrepant. In this temperature range, water-rock interaction has a very high kinetic energy, causing fast reactions within the geological environments, making the prediction of the reaction less possible. In this way, each simulator seeks its own best set of numerical solutions to achieve the equilibrium.

Users must be cautious when choosing geochemical modeling software, as an important factor for choosing a simulator is to know the temperature range that will be used. With the temperature information, the user should make a preliminary study with the available codes to verify the convergence of results to the observed diagenetic reactions.

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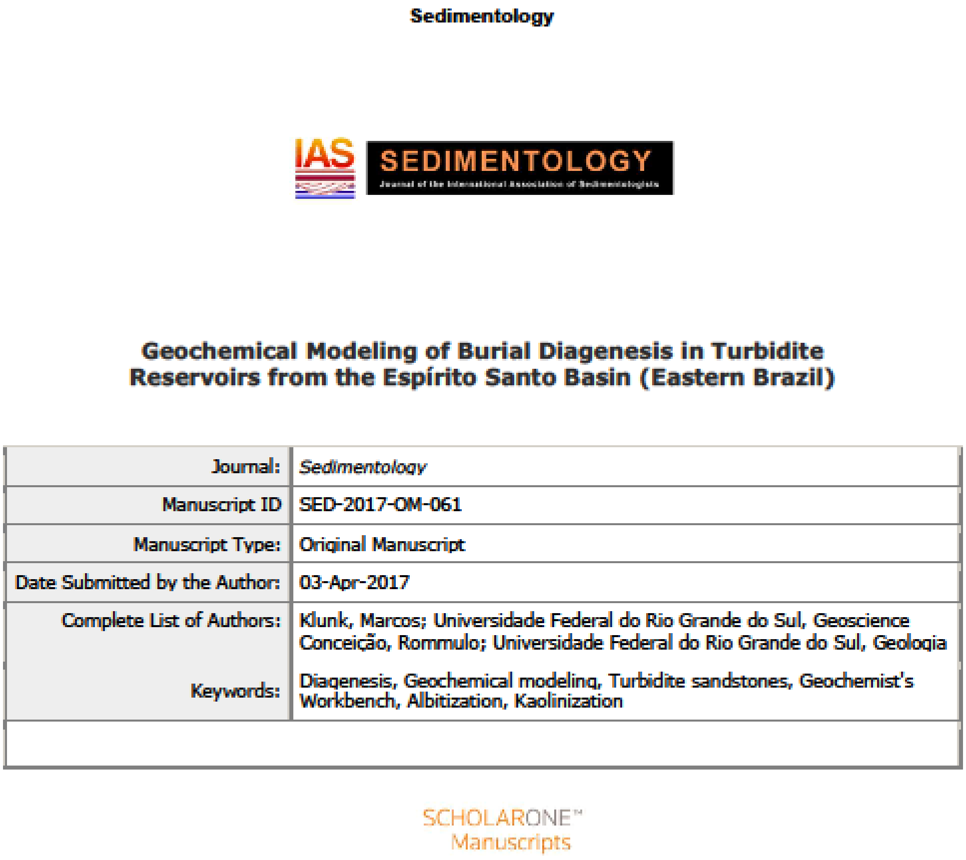

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Geochemical Modeling of Burial Diagenesis in Turbidite Reservoirs from the Espírito Santo Basin (Eastern Brazil)

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Abstract

Diagenetic reactions control the quality of hydrocarbon reservoirs. Geochemical modeling, a useful tool to understand the diagenetic processes, can be performed through computer code based on thermodynamic and kinetic parameters. Performed a comparative study of the diagenetic reactions observed in turbidite reservoirs from the Espírito Santo Basin, using the Geochemist's Workbench (GWB), PHREEQC and TOUGHREACT software. The results allowed the comparison of the geochemical modeling with the petrographic observation of dissolution, albitization and kaolinization processes, as well as the precipitation of calcite and dolomite. The porosity of the sandstones can be predicted in relation to the distribution of dissolution, kaolinization and albitization of feldspars, which significantly changed the essential composition of some samples.

Key-words: Diagenesis, Geochemical modeling, Turbidite sandstones

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1. Introduction

Over the years, the exploration area in oil companies has been facing an increasing geological complexity of the reservoirs, which adds challenges to the prediction of reservoir quality. Therefore, it is necessary to develop and apply new technologies for this purpose. One of them is the geochemical transport and reaction modeling, used for understanding the evolution and distribution of the diagenetic processes and for the characterization and prediction of the quality of oil reservoirs. (Meshri & Ortoleva, 1990; Brenner *et al.*, 1991; Genthon *et al.*, 1997; Giles, 1997). Geochemical modeling uses computational code based on thermodynamic and kinetic parameters. There are several code sources available. Due to the numerical complexity associated with the simulation parameters, each code must be used with caution, and checked against geological and petrological data, in order to better recreate the geological environments.

The development of numerical code applied to geochemical modeling has been the objective of several research groups related to the petroleum industry. An important factor that must be considered in the construction of a geochemical model is the possibility of comparing the results simulated with empirical data, allowing testing the validity and reliability of the code. Once the numerical method has been defined, it is possible to carry out simulations by modifying certain parameters to test their sensitivity when building different geological scenarios.

A scenario is understood as the set of parameters that defines the evolution of the reservoir. A set includes, for example, mineral composition, fluid composition, sequence of mineral crystallization and burial history.

In this study, reproduced the diagenetic reactions observed in turbidite reservoirs from the Espírito Santo Basin, offshore eastern Brazil. The petrographic analysis of this reservoir suggests a diagenetic history divided into four stages: marine eodiagenesis, meteoric eodiagenesis, compactional mesodiagenesis and thermobaric mesodiagenesis (*sensu* Galloway, 1984; Worden & Burley, 2003).

In order to model the diagenesis of these reservoirs, made use of the software Geochemist's Workbench (GWB), PHREEQC and TOUGHREACT. Their source codes are based on advection-dispersion-diffusion models, providing thermodynamic and kinetic parameters to simulate each diagenetic reaction. The three systems were used in batch mode (models that do not consider the mass transport process, referring only to the geochemical reactions), while only GWB and TOUGHREACT were used for dynamic condition models that consider the mass transport processes in one-dimensional flow direction.

The results of the geochemical modeling were compared with petrographic data observed in thin sections and described by De Oliveira et al., (2013). The results of the geochemical modeling showed processes of albitization and kaolinization of detrital feldspars, as well as quartz overgrowth cementation, which occurred during the mesodiagenesis. It was also possible to recreate the conditions of precipitation of calcite and dolomite in the reservoir.

These geochemical results allowed us to predict the porosity of the reservoirs, and the distribution of dissolution, kaolinization and albitization of feldspars that significantly altered the reservoir quality in some areas.

2. Geological context

The Cangoá Field, located in the Espírito Santo Basin, is predominantly characterized by a gas accumulation associated to a small volume of oil, stored in turbidite sandstones of the Urucutuca Formation from the Eocene age. The turbidites are richly composed of feldspars and were deposited and later deformed against a salt dome, which conditioned the structuring of the reservoirs and, potentially, also their diagenetic evolution.

The petrographic analysis and petrological interpretation of the reservoir, which are not the focus of this work, suggest a diagenetic history divided into four stages: i) marine eodiagenesis; ii) meteoric eodiagenesis; iii) compactional mesodiagenesis and iv) thermobaric mesodiagenesis. (*sensu* Galloway, 1984; Worden & Burley, 2003).

The marine eodiagenetic stage comprises the earliest diagenetic processes recognized in the sandstones, including the precipitation of limited pyrite, dolomite and siderite replacing biotite grains, mud intraclasts and filling intraparticle pores in foraminifera bioclasts (De Oliveira et al., 2013). The paragenetic relationships suggest their formation through processes of iron and sulfate reduction by the action of bacteria in marine connatefluids (Berner, 1981; 1984; Morad, 1998).

During meteoric eodiagenesis, the dissolution and kaolinization of feldspars, micas and mud intraclasts, as well as the dissolution of feldspars and the expansion of micas by kaolinite, were quite widespread in the analyzed sandstones.

These processes were promoted by the influx of meteoric waters through the reservoirs when they were still at small depths, a condition that seems to have occurred in other turbidite sandstones of Brazilian basins (Moraes, 1989; Carvalho et al., 1995; Mansurbeg et al., 2012). Such meteoric influx would have been favored by the hydraulic gradient provided by the expressive uplift of the Serra do Mar during the Eocene (Gallagher et al., 1995; Saenz et al., 2005).

During the compactional mesodiagenesis, mud intraclasts and the pseudomatrix generated by their compaction were replaced by microcrystalline silica (De Oliveira et al., 2013). In turbidite sandstones, this process is usually related to the dissolution of radiolaria or other siliceous organisms in the surrounding shales (Sears, 1984; Van Benekon, 1989; Moraes, 1989; Carvalho et al., 1995).

The increasing burial state and pressure dissolution of quartz grains, particularly in contact with mica lamellae and carbonaceous fragments, may have served as source for quartz overgrowths (De Oliveira et al., 2013).

During the thermobaric mesodiagenesis, with the continuation of their burial, the flow of heat and fluids related to the adjacent salt dome began to influence the reservoirs. The convection of fluids derived from the subjacent shales and carbonates through fracture systems generated along the wall of the salt dome promoted the evolution of hot fluids with high Na^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} activities.

The most evident consequence of the action of these fluids in the sandstones is the extensive albitization of the detrital feldspars, particularly the twinned plagioclase and the orthoclase (De Oliveira et al., 2013), due to the proximity of the salt dome.

The precipitation of albite, quartz and late carbonates can be commonly observed in other sandstones associated with salt domes (Hanor, 1987; 1994; 1999; Land et al., 1987; McManus & Hanor, 1988; 1993; Posey & Kylea, 1988; Ranganathan & Hanor, 1988; Evans & Nunn, 1989; Evans et al., 1991; Burley, 1993; Gaupp et al., 1993; Esch & Hanor, 1995; Sarkar et al., 1995; Giles et al., 2000; Haszeldine et al., 2000; Sharp et al, 2001; Enos & Kyle, 2002; Bruno & Hanor, 2003; Archer et al., 2004; Milliken, 2005; Hanor & McIntosh, 2007).

3. Conceptual model of the reservoir

A conceptual model of the reservoir was created based on petrographic, stratigraphic and seismic data (Oliveira et al., 2013). The model is summarized on Fig. 1. The reservoir geometry and the simulation temperature conditions were determined from the burial history and current field conditions.

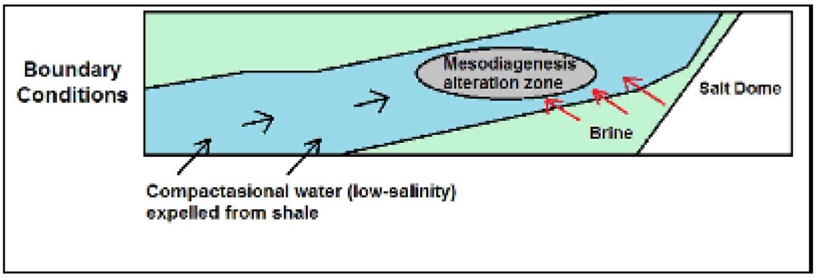


Fig. 1. Conceptual model of the Cangoá Field reservoir in the Espírito Santo Basin (adapted from De Oliveira et al., 2013).

For the formulation of the conceptual model and configuration of the simulations, the petrographic data proposed by De Oliveira et al., (2013) was simplified based on the most important mineral phases that could reproduce each stage of the thermobaric diagenetic history.

The temperatures used in the simulations were based on the thermal and burial history of the reservoir. The mineralogical compositions of the sandstones and shales to be modeled are shown in Table 1.

Table 1. Modeled mineralogical composition of lithologies (as a percentage of the total volume of each rock).

Mineral	Sandstone	Shale
Quartz	46.35	21.15
K-feldspar	8.40	3.2
Plagioclase	12.00	4
Albie	0.3	4.1
Calcite	0.3	2.7
Dolomite	1.10	1.9
Siderite	0	0
Kaolinite	4.35	3.15
Illite	5.5	49.5
Chlorite	0.5	4.5

This conceptual model intends to recreate the thermobaric mesodiagenesis considering the interaction of a highly saline fluid with the sandstone mineralogy. The high salinity of the fluid was acquired after its interaction with the salt dome.

The conceptual model takes into account the percolation of brines from the shales and other lithologies near the turbidite reservoir. This percolation was enhanced due to the thermal contrast caused by the salt dome.

This geochemical modeling predicts the diagenetic reactions of reduction and creation of porosity, which will be used to predict the quality of the reservoir.

4. Primary constitution and composition of the water used for modeling

The restored contents of the main primary constituents were reconstituted based on the paragenetic relations of replacement by diagenetic constituents and dissolution recorded in petrography (Table 1). The original percentages of the major primary constituents were approximated based on the restored values and depositional porosity values corresponding to the grain size sorting of the samples (Table 2). The locations of the main diagenetic constituents were characterized as between intragranular and intergranular, considering that only the latter has a significant impact on porosity and permeability (Table 2).

The compositions of waters used for modeling were:

i) Brackish water from the Gulf of Mexico (Table 3), for the fluids that promoted the meteoric diagenesis processes (dissolution and kaolinization of feldspars, micas and mud intraclasts, expansion of micas by kaolinite);

ii) Water formations from the Gulf of Mexico (Tempel & Harrison, 2000; Table 3), for the fluids expelled by the compacting of the subjacent shales;

iii) Current formation waters in Well B1, for the thermobaric fluid related to the salt dome (Table 4).

Table 2. The average volumes of the main constituents of petrofacies associations recognized in turbidite sandstones of the Espírito Santo Basin.

Constituents	Well – A1	
	Porous (%)	Micaceous (%)
Detrital Quartz	48,42	34,78
Detrital K-feldspar	8,50	9,11
Detrital Plagioclase	12,88	18,89
Micas	0,71	1,78
Carbonate grains	1,46	0,88
Intergranular Albite	0,51	0,89
Intragranular Albite	3,04	4,88
Intergranular Calcite	0,71	0,44
Intragranular Calcite	1,83	0,78
Intergranular Dolomite	0,88	0,22
Intragranular Dolomite	1,33	0,66
Intergranular Kaolinite	0,79	0,33
Intragranular Kaolinite	2,74	3,99
Intergranular Quartz	3,00	2,33
Intragranular Porosity	5,25	6,44
Intergranular Porosity	2,20	2,65
Sum	94,27	89,06

Table 3. Composition of the meteoric fluids and the fluids derived from the compaction of shale used in modeling. Fluids from the edge and Eocene of the Gulf of Mexico. Tempel & Harrison (2000).

Solutes	Meteoric Water (mg/L)	Compaction Water (mg/L)
Na^+	6.30	29.80
K^+	2.30	230.00
Ca^{2+}	15.00	1490.00
Mg^{2+}	4.10	151.00
Cl^-	15.00	476300.00
SO_4^{2-}	11.20	18.00
$SiO_{2(aq)}$	13.10	84.00
Fe^{2+}	1.00	100.00
Al^{3+}	0.01	0.01
HCO_3^-	equil CO_2	equil CO_2
H^+	3.16E-7	3.16E-6
pH	6.50	5.50

Table 4. Composition of the thermobaric fluid related to the salt dome used in the modeling, considering the current formation waters of the Well – A1

Solutes	Sample 1 (mg/L)
HCO_3^-	794.00
Br^-	25.00
Ca^{2+}	3377.00
Cl^-	62517.00
Sr^{2+}	408.00
Fe^{2+}	50.00
I^-	–
Mg^{2+}	345.00
K^+	7640.00
Salinity	103060.00
Na^+	32349.00
SO_4^{2-}	1694.00

5. Software for geochemical modeling

There are many types of software available to simulate geochemical reactions. For this study used Geochemist's Workbench (GWB), PHREEQC and TOUGHREACT.

The GWB was developed by the department of geology of the University of Illinois at Urbana-Champaign in 1978. It performs simple simulations in a short time interval for the calculation of saturation index (using Debye and Hückel Harvie-Møller-Weare models) and distribution of aqueous species. (Bethke, 2002).

PHREEQC is a free software written in the C and C++ programming languages, designed to perform a wide range of geochemical calculations. PHREEQC calculates the saturation index and speciation in batch mode and one-dimensional transport. PHREEQC uses the Pitzer model when the salinity of water is high and outside the application ranges of Debye-Huckel theory. The software uses the numerical integration method, allowing the solution of differential equations that can be generalized for the reconstruction of three-dimensional trajectories. (Parkhurst et al., 1999).

TOUGHREACT was developed to simulate fluid flow non-isothermal multi-component and geochemical transport, in order to investigate problems involving simple and complex geological environments (Xu & Pruess, 1998). TOUGHREACT can also use "batch models", simulating the reactions in a closed system. A number of thermo-physical and chemical processes, which occur in the subsurface, are considered under the aspect of hydrological and geochemical conditions of pressure, temperature, water saturation and ionic strength. The numerical solution to the water-rock interaction is based on the finite difference. These equations are solved by the Newton-Raphson interaction (Pruess, 1991). The activity coefficient is calculated using the Debye-Huckel equation.

6. Results

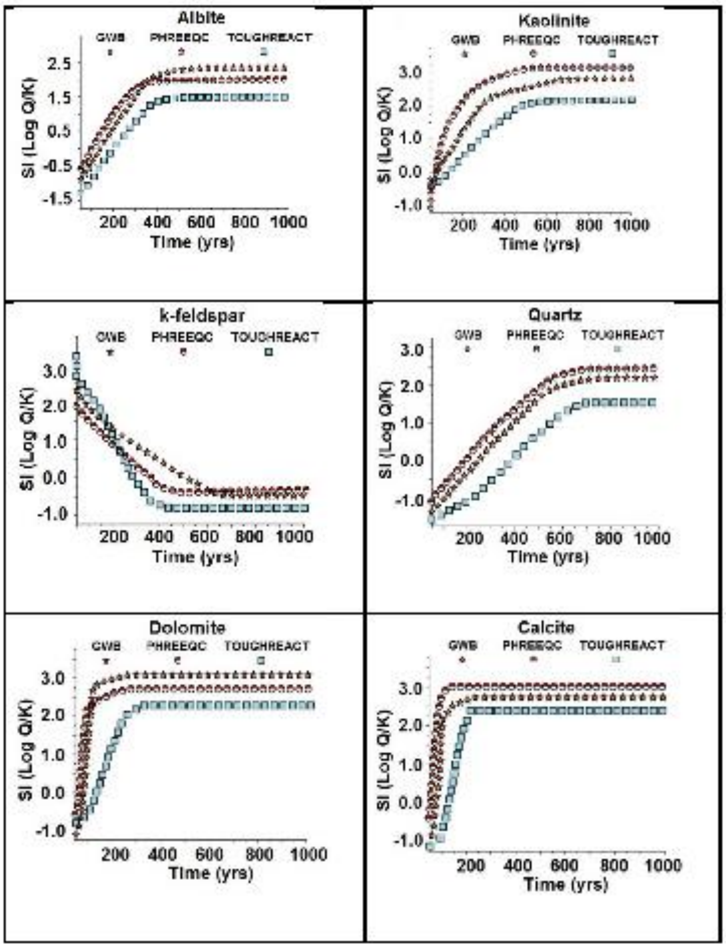
6.1. Simulations in batch mode

Batch mode simulations (Fig. 2) were performed at 120°C, corresponding to the mesodiagenetic conditions where the sandstones were percolated by the compactational flux. The software types used for the geochemical modeling in batch condition were Geochemist's Workbench (GWB), PHREEQC and TOUGHREACT.

Typically, sediments are buried at very low depths and temperatures rise slowly. In addition, the fluid flow rates are also quite low, limiting the mass movement of elements through the rocks. However, over the years, the water-rock interaction tends to achieve chemical equilibrium. The batch mode aims to achieve this steady state, according to the petrographic study. Due to changes in temperature and fluid flow, the water contained in the pores of the rock is not in chemical equilibrium with the mineral rock assembly. The diagenetic reactions are the result of this tendency towards a state of equilibrium never really reached. For this reason, a condition close to a "steady state" is more appropriate to describe the chemical state of rocks and diagenetic fluids.

Fig. 2 shows the progress of the diagenetic reactions for the simulations in batch mode. Initially, minerals are far from equilibrium. Over the time, the minerals reach a "steady state" condition. The three geochemical modeling software demonstrate similar behavior in the precipitation and dissolution of the mineral assembly. Also found intense kaolinization and K-feldspar dissolution.

Observed a process of albitization of plagioclase. The model also shows calcite precipitation and dolomite filling the intergranular pores. Quartz overgrowths are suggested to have co-precipitated with albite. There is a slight discrepancy in the models generated by TOUGHREACT due to the numerical method used in the reactions that occur above 100°C. However, for the GWB and PHREEQC, using a similar numerical method in this temperature range, the plots profiles are practically the same.


Albite
GWB
PHREEQC
TOUGHREACT
SI (Log Q/K)
2.5
1.5
0.5
-0.5
-1.5
200 400 600 800 1000
Time (yrs)
Kaolinite
GWB
PHREEQC
TOUGHREACT
SI (Log Q/K)
3.0
2.0
1.0
0.0
-1.0
200 400 600 800 1000
Time (yrs)
k-feldspar
GWB
PHREEQC
TOUGHREACT
SI (Log Q/K)
3.0
2.0
1.0
0.0
-1.0
200 400 600 800 1000
Time (yrs)
Quartz
GWB
PHREEQC
TOUGHREACT
SI (Log Q/K)
3.0
2.0
1.0
0.0
-1.0
200 400 600 800 1000
Time (yrs)
Dolomite
GWB
PHREEQC
TOUGHREACT
SI (Log Q/K)
3.0
2.0
1.0
0.0
-1.0
200 400 600 800 1000
Time (yrs)
Calcite
GWB
PHREEQC
TOUGHREACT
SI (Log Q/K)
3.0
2.0
1.0
0.0
-1.0
200 400 600 800 1000
Time (yrs)

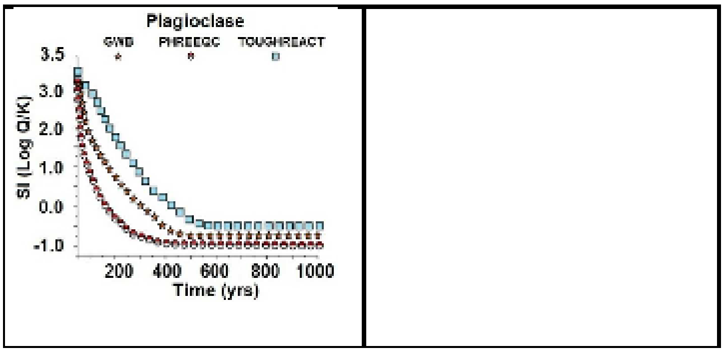


Fig. 2: Mineral saturation for batch mode simulation of a shale at 120°C for 1000 years. The water in start simulation is significantly in non-equilibrium with the rock. Over the time, the composition of the water evolved to approach equilibrium, and the saturations of mineral converge to a "steady state".

6.2. Simulations in 1D

The 1D simulations (Figs 3-9) were performed using the previous results of the batch mode simulations. The simulation domain used has a length of 100 meters at 140°C (temperature referring to the thermobaric mesodiagenesis). The numerical cell resolution has 1 grid per meter. The first part of the simulation domain consists of 10 meters of shales and 90 meters of sandstone. These simulations reveal that, for a short time, the minerals do not reach the steady state. With the evolution of the water pushing the shales towards the sandstones, the minerals react with the environment, achieving stability as the simulation time goes by.

The modeled stability of minerals is assumed to acquire water-rock interactions from 600 years ago. The GWB and TOUGHREACT exhibit similar behaviors for the evolution of the interaction system. In the simulations in 1D, the results show similar behaviors to those observed in the petrographic analysis (De Oliveira et al., 2013).

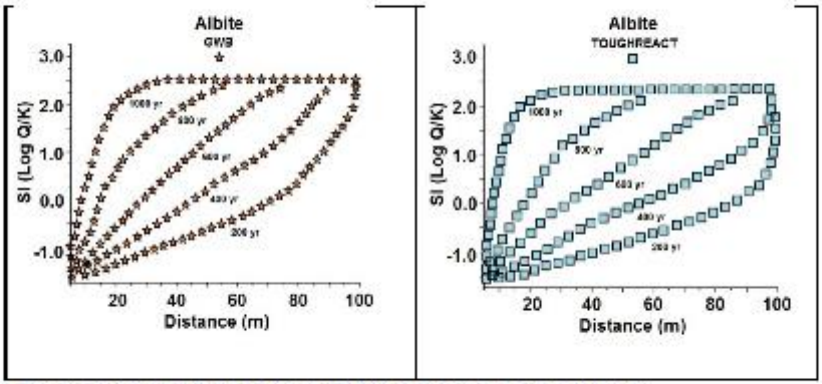


Fig. 3: Saturation index of albite in 1D simulation (shale-sandstone system).

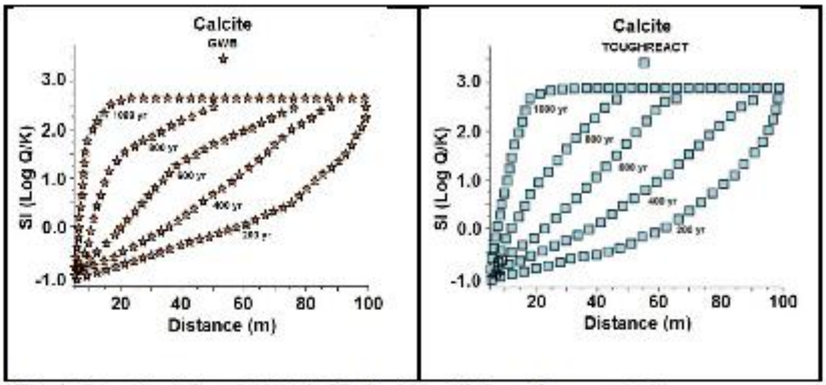


Fig. 4: Saturation index of calcite in 1D simulation (shale-sandstone system).

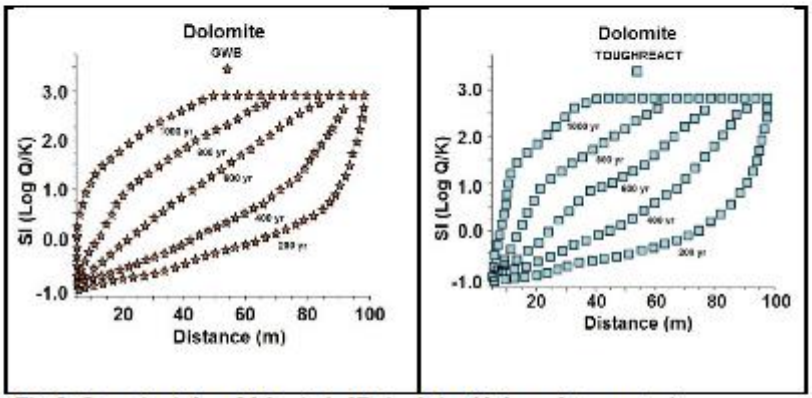


Fig. 5: Saturation index of dolomite in 1D simulation (shale-sandstone system).

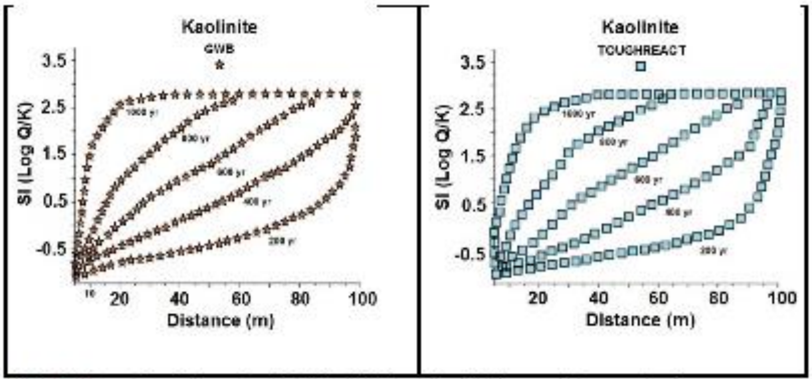


Fig. 6: Saturation index of kaolinite in 1D simulation (shale-sandstone system).

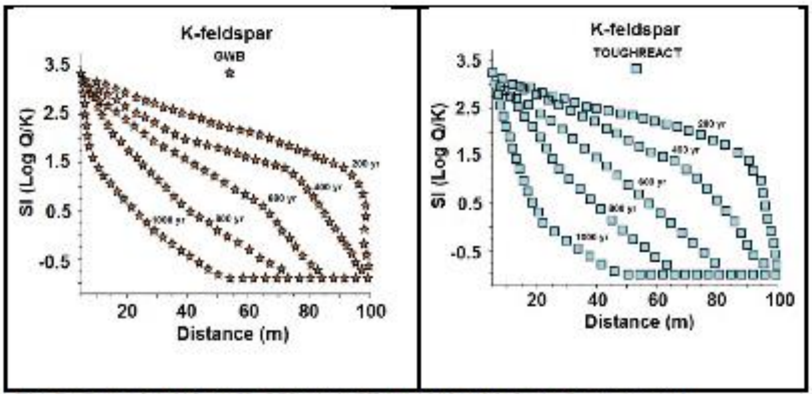


Fig. 7: Saturation index of k-feldspar in 1D simulation (shale-sandstone system).

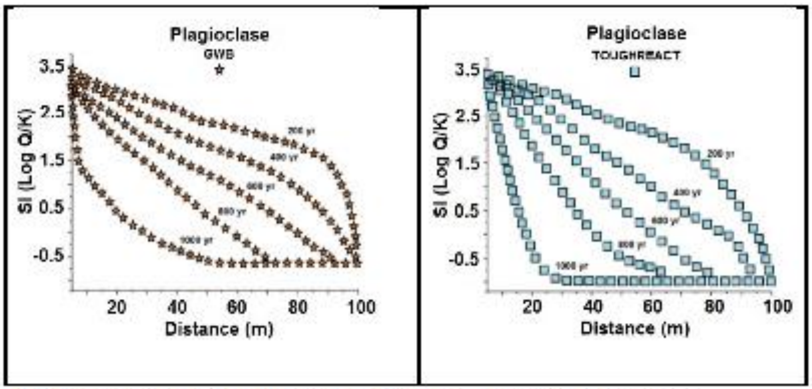


Fig. 8: Saturation index of plagioclase in 1D simulation (shale-sandstone system).

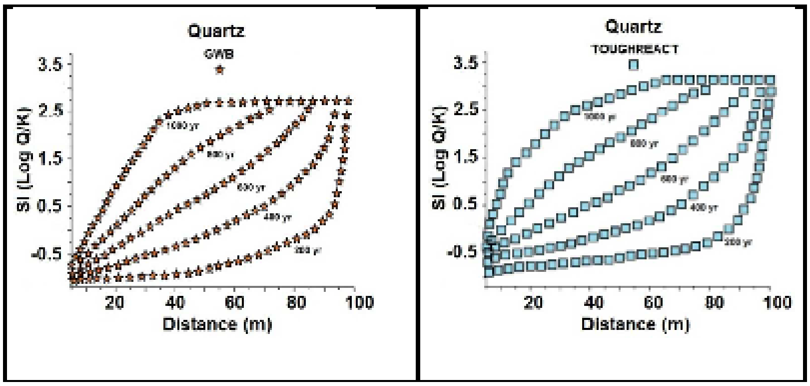


Fig. 9: Saturation index of quartz in 1D simulation (shale-sandstone system).

7. Discussion

The simulations modeled the effect of the circulation of fluids modified by the interaction with a salt dome near the turbidite reservoirs, during the thermobaric mesodiagenetic regime.

Petrographic studies were used to establish the current and the original compositions of sandstones, as well as the evolution of the diagenetic processes.

To build the simulations, we used the average composition of the sandstone reservoirs of Well – A1. Also used the mineral assembly in the end of the meteoric diagenesis and of the compactional mesodiagenesis, and the beginning of the thermobaric mesodiagenesis, based on the petrographic characteristics and burial history.

The meteoric eodiagenetic stage is marked by an intense dissolution and kaolinization, in their entirety, of silicate grains, into detrital feldspars. The authigenic carbonate, silicification of mud intraclasts, and some of the volume of the quartz growth are the typical diagenetic products of the compactional mesodiagenesis, characterized by the connate fluid flow coming from the surrounding shales.

The last stage, the thermobaric mesodiagenesis, was controlled by the effects of the brine percolation from the salt domes near the turbidite reservoirs. Typical diagenetic products of this interaction were the intense albitization of feldspar and the quartz overgrowths around the detrital grains (De Oliveira et al., 2013).

The developed geochemical model is related to the last stage of the diagenesis. While the meteoric diagenesis and the compactional mesodiagenesis decrease the sandstone porosity, the thermobaric mesodiagenesis introduced larger porosity variations within the reservoirs. This justifies the choice of focusing the simulation on this stage and not on the others.

Initially the simulations were performed in batch mode (Fig. 2) due to water instability. Once a steady state is reached, these chemically stable waters with the rock can be modeled. From the shales, the brine percolates the sandstone, forming a reactional front inside the reservoir.

Depending on the reactions observed in the geochemical modeling, a mineralization pattern can affect the quality of the reservoir. For the prediction and analysis of the reservoir quality, a large number of simulations were performed, differing in water composition, temperature and fluid flow rate. The results of all the simulations represent a statistical probability which can identify the significance of these parameters in reservoir quality.

Regarding the geochemical modeling software used in the simulations in batch mode, can identify similarities in the profiles generated by the precipitation and dissolution of mineral assemblage. The slight differences observed in the simulations depend on the numerical methods used by each simulator, but they do not show discrepancies among the results. To take into account that both the kinetic and thermodynamic parameters are affected by high temperatures.

Each simulator solves the equations based on these parameters. GWB and PHREEQC reproduce the diagenetic reactions in batch mode more precisely by using numerical approximations at temperatures of 120°C. The 8th degree polynomial, present in the database both simulators, solves the equations incisively.

However, TOUGHREACT reproduces the diagenetic reactions somewhat differently by using the temperature parameter of 120°C, which causes a slight instability in the numerical method because of the kinetic and thermodynamic parameters applied.

The 1D simulations are shown in Figs 3 to 9. The plots show the mineral phases of saturation at five different times (200, 400, 600, 800, and 1000 years) by using the GWB and TOUGHREACT. In general, with the time step, the minerals reach a steady state. Due to the high temperatures (140°C) of the thermobaric mesodiagenesis, the saturation indices of the mineral assembly became slightly different.

The precipitation of kaolinite (Fig. 6), filling the secondary porosity formed by the dissolution of feldspar grains (Fig. 7), was recognized in several samples partially cemented by carbonates. The feldspar grains in the sandstones of the Urucutuca Formation are largely albitized.

The models predict the dissolution of plagioclase (Fig. 8), and K-feldspar (Fig. 7) with albite precipitation (Fig. 3). The precipitation of calcite (Fig. 4) in sandstones occurs easily, since the calcite solubility decreases with the temperature increase. The precipitation of dolomite (Fig. 5) occurs after the calcite.

The quartz precipitation (Fig. 9) represents the first mesodiagenetic event of importance in the studied sandstones.

The silica source for the cement precipitation can be related to the (i) pressure dissolution of quartz grains; (ii) clay transformations during burial; (iii) kaolinization or dissolution of feldspars in the sandstones; and (iv) dissolution of quartz grains in the shales.

8. Conclusions

The eocene turbidite sandstone reservoirs of the Espírito Santo Basin, Brazil, had their diagenetic history developed under the eodiagenetic and mesodiagenetic regimes. The relationships between the events of cementation, dissolution, and replacement in the sandstones allow us to establish the sequence of diagenetic events.

The marine eodiagenetic regime was characterized by the dissolution of unstable minerals and the precipitation of microcrystalline calcite, pyrite and K-feldspar. The meteoric eodiagenesis was promoted by the circulation of meteoric water, causing the dissolution and kaolinization of feldspars and micas.

Under mesodiagenetic conditions, the sandstones were percolated by compactational and thermobaric fluids, resulting in different diagenetic processes, including quartz overgrowths, plagioclase dissolution, cementation by calcite and dolomite, the dissolution of feldspars, the precipitation of kaolinite and albitization of feldspars.

The porosity of the sandstones is largely of secondary origin, represented by intergranular, intragranular and fracture types.

Generally, the original composition of the sandstones formation has been modified by a set of diagenetic processes, including the dissolution of unstable minerals, the replacement of framework grains, the precipitation of carbonate and the albitization of feldspar.

The simulations performed with the geochemical modeling software Geochemist's Workbench (GWB), PHREEQC and TOUGHREACT were used to predict the diagenetic reactions observed in the turbidite sandstone reservoirs of the Cangoá Field, Espírito Santo Basin, Brazil. This work was important to understand the diagenetic alteration of sandstones exposed to a saline water flow.

The building of a conceptual model allowed the configuration of geochemical models based on seismic, stratigraphic and simplified petrographic data. The burial history and current data of the field allowed the construction of the reservoir geometry and temperature conditions used in the simulations.

Using simulations in batch mode and 1D, it was possible to observe the behavior of the minerals when subjected to various reaction conditions. Parameters like the saturation index, and the porosity change allowed the understanding of diagenetic reactions in a geological environment.

The simulations in batch mode enabled the formation waters to achieve the steady state, which allowed us to use the equilibrated compositions for the simulations in 1D. The time required for the shale and sandstones to reach the steady state depends on the grain size of each lithology.

The simulations in 1D reveal an intense albitization accompanied by the precipitation of kaolinite and the dissolution of plagioclase.

This approach provides a tool for estimating the intensity of albitization in relation to the inflow of saline fluid into the reservoirs. These qualitative observations obtained provide empirically controlled rules that can be used in exploration and production operations in the petroleum industry.

The results also indicate alterations of the sandstones, with the loss of porosity, significant albitization and significant amounts of calcite and kaolinite precipitated. The porosity decreases along a reaction zone when the water from shale comes in contact with the sandstones.

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3. CONCLUSÃO

Os dados obtidos ao longo do desenvolvimento desta Tese de Doutorado, apresentados sob a forma de artigos científicos, e integrados com os dados disponíveis na literatura permitem concluir sobre as hipóteses elencadas na caracterização do problema científico (item 1.2 Problema Científico).

A hipótese de que podemos modelar as fases diagenéticas existentes em um arenito reservatório para prever a qualidade dos mesmos como um potencial acumulador de óleo ou gás traz confiabilidade na construção de modelos geológicos.

O levantamento de dados sobre os códigos de simulação numérica, bem como o estudo inicial de modelagem geoquímica, utilizando o PHREEQC, GWB e o TOUGHREACT aplicado em um sistema petrolífero, permitiu um maior entendimento para a formulação de um modelo conceitual para os demais problemas geológicos encontrados ao longo deste trabalho.

Sabemos que a modelagem geoquímica somente é útil, se tivermos bons dados cinéticos e termodinâmicos. Desta forma podemos criar modelos simplificados com maior precisão e confiabilidade. Dados estratigráficos e petrográficos possibilitam recriar as condições reacionais do ambiente geológico.

Reações diagenéticas são afetadas pela temperatura do meio reacional. Isto tem consequências diretas na escolha dos softwares de modelagem. Para baixas temperaturas, tanto o GWB como o TOUGHREACT possuem suas particularidades nos métodos numéricos. A precisão dos resultados, em certos casos, pode ser inferior quando comparado com a realidade das reações diagenéticas na formação geológica.

Para temperaturas de 100 a 140°C, temos o ambiente ideal para reproduzir as reações diagenéticas. Os softwares utilizam métodos numéricos estáveis com maior convergência de resultados, aumentando a precisão ao recriar um ambiente geológico. Acima desta faixa de temperatura, os simuladores encontram dificuldades para resolver as equações químicas proveniente das reações diagenéticas.

Os experimentos em laboratório seguido de uma modelagem geoquímica nos, possibilitou fazer um comparativo daquilo que encontramos na realidade com a previsão feita pelo modelamento. Estes resultados geram uma maior credibilidade e confiabilidade na modelagem geoquímica, desde que utilizamos os parâmetros cinéticos e termodinâmicos de boa qualidade. O importante é definir uma faixa de temperatura ideal para cada simulador, levando em conta que o método numérico é sensível nas mudanças de temperatura.

A construção de um modelo conceitual e a previsão das alterações diagenéticas ocorridas em um reservatório da Bacia do Espirito Santo, tendo como base os arenitos turbidíticos da formação Urucutuca fornecem uma compreensão qualitativa da alteração diagenética dos arenitos quando expostos ao fluxo de águas salinas dos lutitos. A correlação feita com os eventos diagenéticos observados nas lâminas delgadas e o modelamento geoquímico foi de suma importância para validar os modelos.

Para a escolha certa de um software de modelamento geoquímico, o usuário precisa realizar vários testes. Desta forma, os resultados obtidos formarão um perfil que revelará a tendência de precipitação/dissolução de minerais. Um estudo comparativo destes perfis mostrará qual software se aproxima com a realidade das reações diagenéticas.

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