CO₂-BRINE-ROCK INTERACTIONS IN RESERVOIR CHALK ROCK – A COUPLED EXPERIMENTAL AND NUMERICAL APPROACH FOR OBTAINING HYDROCHEMICAL RESULTS AT RESERVOIR CONDITIONS

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ABSTRACT

Sampling and analysis of water chemistry in reservoir condition experiments with high CO_2 pressures is challenging since CO_2 can easily degas from the samples and cause changes in the chemical composition before chemical analyses are performed. In the literature, water samples during dynamic experiments for chemical analyses are often obtained behind a back pressure (BP) regulator located at the downstream end of the flooding specimen. As a consequence, chemical samples are obtained at a lower pressure (often atmospheric pressure) via the BP regulator. Another approach is to sample directly from the device where reservoir conditions are applied (e.g. core holder or batch) and subsequently carry out chemical analyses or preserve samples "as fast as possible" after sampling. In both approaches, there is essentially no control on the CO_2 pressure and therefore CO_2 degassing during the sampling procedure may cause both precipitation of carbonate and an increase in pH. As a result, the measured chemical composition may differ substantially from the true chemical composition at reservoir conditions.

We present a novel methodology that, on the basis of obtaining a consistent set of hydrochemical data at one set of well-known physical conditions (CO_2 pressure and temperature), enables the estimation of true reservoir conditions by the application of numerical calculations with the hydrogeochemical code PHREEQC. The technique is demonstrated for an experimental study where reservoir chalk was flooded with either CO_2 saturated water or slugs of CO_2 and seawater in a WAG (water alternating gas) scheme at reservoir conditions. The methodology is validated by various independent check calculations such as comparison of forward modeling results with measured results and carbonate mass balance calculations.

At present, the methodology is considered applicable for flooding of chalk material where the dominant chemical reactions taking place are dissolution/precipitation of calcite and gas/water equilibrium with a CO_2 gas phase. In the case of a water-alternating-with-gas (WAG) flood, the numerical calculations may be refined by application of a true 2-phase numerical code such as TOUGHREACT in a 2D or 3D model.

INTRODUCTION

Typically, CO_2 -EOR is carried out as a water-alternating-with-gas (WAG) process that involves injection of slugs of CO_2 followed by water floods. When CO_2 is injected, high gas saturations are expected in the near-injector region, and eventually complete dry-out and salt precipitation may occur. When water is injected, gas saturations decrease and CO_2 is dissolved in the water, thereby providing potential for dissolution of minerals. Overall, coupled chemical and physical processes such as dissolution, precipitation, porosity and permeability changes may occur. These processes may be responsible for observed injectivity problems (Ross et al., 1982; Grigg and Svec, 2001) and well impairment, or may cause changes in rock mechanical properties (Madland et al. 2006).

In order to provide some insight to the possible mechanisms giving rise to injectivity losses as well as to rock mechanical issues, several laboratory experiments have been performed previously (Grigg and Svec, 2001; Egermann et al., 2005; Madland et al., 2006). Grigg and Svec (2001) studied the physical effects of the CO₂-WAG process in limestone and dolomite rock and observed dissolution features in all cores exposed to WAG fluids. Thus, carbonate and anhydrite dissolution were responsible for changes in core permeability and porosity. In agreement with these findings, Madland et al. (2006) furthermore observed an increased creep rate after treating outcrop chalk with CO₂ or carbonated water. In addition, Egermann et al. (2005) showed that the flow rate and composition of brine initially present in cores play a major role in fluid-rock interactions. Thus, formation of various non-uniform dissolution facies and in some cases reprecipitation and permeability reduction were observed.

However, in most previous experiments, water samples for chemical analyses were often obtained behind a back pressure (BP) regulator located at the downstream end of the flooding specimen. As a consequence, CO_2 degassing occurs during the sampling procedure. This may cause both precipitation of carbonate and an increase in pH, and as a result the measured chemical composition may differ substantially from the true chemical composition at reservoir conditions. For mechanistic and geomechanical purposes it may be sufficient to approximate the knowledge about chemical conditions at reservoir conditions by such a procedure. However, in the case where the application of chemical analyses in experiments is used to generate data and knowledge for the calibration of numerical models for regional scale modeling, it is essential that the true chemical state at the applied reservoir conditions of the experiments can be estimated.

In this paper, we present a methodology where the CO_2 pressure is measured during the sampling procedure in flooding experiments with chalk samples at reservoir conditions. This enables the estimation of the true chemical state at reservoir conditions by the application of numerical calculations using PHREEQC (Parkhurst and Appelo, 1999). The laboratory experiments consisted in the injection of CO_2 -WAG as well as carbonated water at reservoir conditions in order to investigate the effect of CO_2 flooding on chalk dissolution and petrophyscial changes in near-well bore as well as far-field regions at reservoir conditions.

THEORETICAL CONCEPT

The reservoir chalk used in the present study consists mainly of low-magnesium calcite $(Ca_{1-x}Mg_xCO_3)$ – hereafter referred to as 'calcite' for simplicity. If we assume that precipitation of secondary precipitates such as gypsum (CaSO₄) is minimal, the main chemical reactions that are expected to take place both during flooding and sampling in the laboratory may be described by the following overall reaction:

$$CO_{2(aq)} + CaCO_3 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^{-}$$
(1)

From this equation we expect that flooding of the reservoir chalk samples, either with carbonated water or according to a CO_2 -WAG scheme, will drive reaction (1) towards the right and thereby cause dissolution of calcite and increased alkalinity and Ca concentrations in the chalk sample. Furthermore, the dissolution of CO_2 in the pore water will give reason to a decrease in pH as compared to the initial pH of the seawater used for the flooding purpose. This is in good agreement with what has been observed in previous similar studies (Grigg and Svec, 2001; Egermann et al. 2005).

The chemical analyses carried out as part of the present study comprise pH, alkalinity in the form of HCO_3^- (Appelo and Postma, 2005), Cl⁻, $SO_4^{2^-}$, Ca and Mg concentrations. None of these were possible to carry out at the pore pressures applied during the experiments (2,500 and 4,500 psig, respectively). Therefore, collection of water samples required a depressurisation step. During the depressurisation of the water sample, reaction (1) is driven towards the left and degassing of CO_2 from the water sample takes place. This causes some precipitation of calcite, and thereby both the alkalinity and the Ca concentration. Furthermore, the degassing of CO_2 causes an increase in the pH as compared to the true reservoir condition pH.

In the case where the chemical dataset after the depressurisation step is obtained at the same – or nearly same – physical conditions (temperature and pressure), and if the CO_2 pressure is measured at the same time, the dataset may be considered to be consistent. Thereby, it is possible to carry out a chemical speciation calculation of the obtained sample with a numerical code – in this case PHREEQC – and subsequently use equation (1) to estimate the chemical state at reservoir conditions. The latter step involves the assumption that calcite equilibrium is present in the pore water of the tested chalk sample at reservoir conditions. In the present case, the numerical calculations with PHREEQC comprised a forward step/batch modelling of the experiments.

A further check on the validity of the numerical calculations involved estimating the amount of calcite expected to dissolve during the experiments from the numerical results and comparison with the actual weight losses (before and after) of the chalk samples as a result of the flooding experiments.

ANALYTICAL PROCEDURE

Porous Media and Fluids

Chalk reservoir plugs sampled from the same geologic formation were used for the experiments. Each plug had a diameter of 3.8 cm and a length of approximately 7.5 cm. Based on CT scanning images and conventional core analysis (CCAL) data, core plugs with similar porosity and permeability were selected and used in the experiments (Table 1). A new plug was used for each experiment. The brines used were synthetic seawater (SW – 3.5 wt.% salinity) and formation water (FW – 6.1 wt.% salinity) prepared in the laboratory. CO_2 with purity 99.9% was used as the gas phase. Since the main purpose of the experiments was to evaluate the novel sampling procedure and because the applied numerical code did not have the possibility of incorporating an oil phase, the experiments were carried out in the absence of an oil phase.

Plug	Porosity (%)	PV (ml)	Klink. Perm. (mD)	S _{wi} (%)
Scenario 1 – Carbonated water flooding				
17A	32.57	26.94	1.36	100
19A	30.66	25.59	1.49	100
Scenario 2 – CO ₂ /seawater WAG flooding				
19B	26.81	22.05	0.99	100
22B	29.31	24.34	1.04	100

Table 1. Overview of experiments and petrophyscial properties of chalk plugs used in the experiments.Data are prior to experiments.

Experimental Set-Up

An experimental rig was designed and built specifically to carry out the flooding of plugs (Figure 1). The core of the flooding rig is a high temperature oven equipped with two core holders. The set up enables flooding either directly through the target plug specimen of a specific flooding scenario or flooding with pre-saturation with CaCO₃ at the required pressure and temperature by flooding through a "dummy" plug core holder prior to flooding the target plug specimen of a specific scenario.

Also located inside the oven are three ProLight Ti-690-100 MB portable PVT piston cylinders. Two of these serve as containers for the delivery of liquid/gas at the upstream end of the plugs, while the third PVT cylinder located inside the oven is used for reception of liquid/gas (waste tank) when flooding is carried out as well as for maintaining the pore pressure in the flooded plug specimen.

The confining pressure and the pressure and flow of the PVT piston cylinders are controlled by high precision Quizix Q-5000 piston pumps using distilled water as pressure media. Immediately upstream and downstream the core holder with the target plug specimen, 10K psi Sensata pressure transducers are placed in order to obtain the differential pressure across the target plug specimen during the entire flooding procedure.



Figure 1. Sketch of the experimental rig used for the experiments.

The system for obtaining water samples for chemical analyses is located downstream the target core holder. The system consists of two primary sample loops constructed in 1/8" tubing (316 SS), each approximately 10 mL in volume, enabling continuous collection of water samples at reservoir conditions for every 10 mL of target plug specimen flooded. Downstream the primary sample loops a secondary sample cylinder with larger volume (typically 125-300 mL) can be connected. Thus, when the water sample is transferred from the primary loop to the secondary sample cylinder, the pressure decreases and degassing of CO₂ occurs in the secondary sample cylinder. This enables the collection of the consistent set of chemical data (CO₂ pressure, pH, major cation/anion concentrations) so that numerical calculations can be carried out as part of the post-processing of data.

The CO₂ pressure in the secondary sample cylinder is measured with a 1K psi Sensata pressure transducer and pH is measured with a pH electrode (PRO140J-5M-BNC) connected to an Adwa AD-1030 pH-meter. The water sample for further chemical analyses (pH, Ca, Mg, alkalinity, Cl^- , SO_4^{2-}) was taken as fast as possible (typically

within 0.5 - 1 minute) directly from the secondary sample cylinder. Samples for Ca and Mg analyses where preserved using 1% suprapur 14 M HNO₃ while anion samples were cooled at 5°C until analysis. All samples were filtered through 0.2 µm Satorius cellulose acetate (CA) filters. Alkalinity was measured on both filtered an unfiltered samples immediately after retrieval. Unfiltered alkalinity samples were subsequent to the alkalinity titration analysed for Ca and Mg content in order to evaluate whether fines were mobilised during the flooding process. In general, this did not seem to be the case.

The tubing used for the rig is 1/8" tubing and all valves, tees, and other hardware are Autoclave Engineering (AE) equipment, except valves in the sampling system being Vindum Engineering CV-210 valves that can be operated without opening the oven. At the upstream end of the core holders tubing and valves are Hastelloy-C, while at the downstream end tubing is 316 SS. By placing most of the equipment inside the oven, the major part of the experiments can be carried out without opening the oven, thereby pressure and temperature fluctuations are minimized during the experiments.

Preparation of Plugs with Formation Water (FW)

The plugs were cleaned with toluene and methanol until effluent samples were colourless and free of salt. Afterwards, the plugs were saturated with FW – first by vacuum saturation and subsequently by pressure saturation at 1,600 psig for 2 days.

Procedures for Dynamic Injection with CO₂ and Carbonated Water

Two different scenarios of CO_2 flooding were performed, each carried out as parallel experiments with two different plugs (Table 1). The first case (Scenario 1) involved injection of CO_2 saturated water at supercritical CO_2 conditions. The experiments were carried out at a pore pressure of 2,500 psig, a confining pressure of 3,000 psig, and a temperature of 75°C. This scenario was performed to mimic far-field/water flooded regions where CO_2 gas is expected to be dissolved in the water phase.

The second scenario (Scenario 2) involved the injection of alternating slugs of CO_2 followed by SW. Four (4) cycles of CO_2 followed by SW were injected. The experiments were performed at a pore pressure of 4,500 psig, a confining pressure of 5,000 psig and a temperature of 25°C. This case represented the situation at the near-well bore area where there has been extensive cooling due to water flooding.

In both cases, the flooding processes were preceded by injecting 2-4 pore volumes (PV) of SW to mimic the present day water flooding to some extent. In reality, near-well regions have probably been water flooded by even larger amounts of PV, while for far-field regions the number of water flooded PV are probably lower. However, it was in both cases chosen to pre-flood by 2-4 PV of SW in order to rule out possible effects from the water flood when comparing results from the two scenarios. Likewise, in the eventual stage of both scenarios, the plugs were flooded with at least 4 PV of calcite saturated SW (via flooding through the "dummy" plug) to remove residual CO_2 in the plugs before demounting from the core holders was carried out.

Analytical Methods

The inductive coupled plasma mass spectrometry (ICP-MS) method was used to analyze for Ca and Mg in the produced fluids. Cl⁻ and $SO_4^{2^-}$ contents were analysed spectrophotometrically, though the results are not presented in the present paper. The pH of the produced fluids was measured on-line with a pH meter. Gran-titration with 0.1 M HCl was used to determine the alkalinity (HCO₃⁻) (Appelo and Postma, 2005).

Numerical Calculations and Post-Processing

As mentioned, numerical calculations were performed using the hydrogeochemical code PHREEQC (Parkhurst and Appelo, 1999). Two sets of calculations were carried out:

- One set, in order to validate the consistency of CO₂ sensitive chemical data measured partly in the secondary sample cylinder (CO₂ pressure and pH) and partly on samples preserved or measured immediately after sampling (Ca and alkalinity (HCO₃⁻)). In these calculations, the measured chemical composition was used as input to a speciation modeling of each single water sample. The only parameter not used as input is the CO₂ pressure which is calculated on the basis of the remaining data. By comparing this calculated CO₂ pressure with the pressure measured in the secondary sample cylinder, it is possible to evaluate the consistency of our dataset; i.e. if there is good agreement between the measured and calculated CO₂ pressure, it is considered that the dataset is consistent. In addition to the consistency check, the speciation modeling provides information about the saturation state with respect to calcite of the water sample taken from the secondary sample cylinder.
- The other set of numerical calculations are used to estimate the true reservoir condition chemical concentrations in the flooded plugs at the operating conditions of the experiments. In this set of calculations, the pH, Ca concentration and alkalinity are calculated at 3 stages of the experiment: 1) at the initial SW flooding; 2) at reservoir conditions; and 3) at the conditions measured in the secondary sample cylinder. The calculation is carried out as a batch-like forward model of the experiments and the following input and assumptions apply for each stage:
 - 1) the input for the SW calculation is the known chemical composition of the SW and the assumption is that calcite equilibrium is present in the plug;
 - the input for the reservoir condition calculation is the chemical composition calculated from stage 1 together with the temperature applied in the experiment. The assumption is that calcite equilibrium is present in the plug and that the CO₂ pressure is equal to the pore pressure in the experiment during the entire flooding;
 - 3) the input for the sample point calculation is the chemical composition calculated from stage 2 together with the sampling temperature, the measured CO₂ pressure, and the saturation state with respect to calculate as calculated from the speciation calculations. No further assumptions are made for this calculation.

Since the mass balance for the flooded plugs is calculated on the basis of measured weights before and after the experiments, the second set of numerical calculations offers two independent measures on the validity of the applied methodology; i.e. 1) by comparison of measured and calculated chemical composition of the water at the sampling point and 2) by comparison of the measured mass balance with the expected weight loss as calculated from the estimated reservoir condition hydrochemistry.

RESULTS AND DISCUSSION

Consistency of Dataset

For all plugs flooded, the calculated CO_2 pressure on the basis of the measured chemical composition at sampling conditions correspond well with the actually measured CO_2 pressures in the sampling system (Figure 1). In general, the difference between measured and calculated pressures is less than 0.5 bar (~7.3 psi). The most stable CO_2 pressures of 2 bar (~29.0 psi) and the best correspondence is observed for plugs 17A and 19A flooded with carbonated water as part of Scenario 1 (Figure 2a and b) while a more fluctuating pattern together with a higher sampling CO_2 pressure around 3 bar (~43.5 psi) is observed for plugs 19B and 22B flooded by following the WAG scheme in Scenario 2 (Figures 2c and d). This is a natural consequence of the higher pore pressure applied in Scenario 2 as well as the WAG nature of the experiments.



Figure 2 Measured and calculated CO₂ pressures (in bar) in the secondary sample cylinder during flooding of plugs in Scenario 1 (a and b) and Scenario 2 (c and d), respectively.

The largest deviations between measured and calculated CO_2 pressures at sampling conditions are observed for plug 19B between 15-20 PV flooded (see Figure 2c). These deviations are most likely caused by slightly erroneous pH measurements in this period where occasionally the pH electrode had some difficulties handling the high CO_2 pressures occurring under Scenario 2. However, a post experimental sensitivity analysis on the parameters involved in the numerical calculation (salinity, alkalinity, Ca and Mg concentrations and pH) showed that small errors in the pH measurement may cause relatively high variations in the corresponding calculated CO_2 pressure. Thus, keeping all other parameters constant, a change in the measured pH by 0.1 pH unit - which is the estimated uncertainty on the measurement – gives rise to a change in the calculated sampling CO_2 pressure of approximately 0.5 bar. Taking this into consideration, we believe that the good agreement between measured and calculated CO_2 pressures at sampling conditions demonstrate that the experimental chemical dataset obtained is consistent and can be used for calculations where the true reservoir conditions chemical state of the water samples is estimated/are needed.

Scenario 1 – Flooding with Carbonated Water

The good agreement between the measured alkalinity, pH, and Ca-concentration for plugs 17A and 19A flooded during Scenario 1 illustrates well the capability of the experimental set-up to produce reproducible chemical data during flooding with carbonated water (Figures 3a and b). The evolution in the measured chemical composition reflects the flooding scheme followed. Thus, the initial phase with decreasing Ca-concentration, slightly decreasing alkalinity and increasing pH (0-3.5 PV) corresponds to the initial SW flooding. This phase is followed by a phase where the Ca-concentration and alkalinity initially increase and a corresponding drop in pH takes place. Subsequently, all measured parameters are more or less constant for a long period (3.5-15 PV). This phase corresponds to the phase, where flooding with carbonated water takes place and dissolution of calcite occurs in the flooded plugs. Finally, the phase with flooding with SW through the "dummy" plug is illustrated by the eventual drop in alkalinity and Ca-concentrations and corresponding increase in pH (15 PV – termination of experiment).

In addition, Figures 3a and b show a comparison of the batch forward modelling results with the measured chemical data. As shown, there is a good agreement between the batch calculations and the measured chemical dataset prior to flooding with CO_2 saturated water (step 1) as well as with the measured chemical composition during flooding with CO_2 saturated water (step 3). As expected, the estimated reservoir condition Ca-concentration and alkalinity (step 2) are higher than the measured values. Thus, the estimated reservoir condition Ca-concentration is 1,850 mg/L compared to an average measured Ca-concentration of 1,200 mg/L. Likewise, the estimated alkalinity at reservoir conditions is 70 mmol/L while the measured alkalinity is around 50 mmol/L. In correspondence with the much higher CO_2 pressure at reservoir conditions, the estimated pH at reservoir conditions is as low as 4.8 compared to the average measured pH of 6.1.



Figure 3 Modelling results (solid lines for step 1, 2, and 3) compared with measured chemical composition in the secondary sample cylinder during Scenario 1. **a**) Ca-concentrations (hatched lines are concentrations in SW and FW, respectively); and **b**) pH (numerical results blue) and alkalinity (numerical results orange).

In order to check the reliability of the estimated reservoir conditions in the plugs, the expected amount of calcite dissolved was estimated from the total volume of carbonated water flooded through the plugs and the estimated Ca-concentration of 1,850 mg/L. The weight losses were estimated as 1.29 g and 1.23 g for plugs 17A and 19A, respectively. This corresponds reasonably well with the measured weight loss of 1.71 g and 1.25 g for plugs 17A and 19A, respectively taking into account that the grain loss in this type of experiments is typically in the order of 0.05-0.15 g (GEUS Core Laboratory, unpublished data). The fairly large deviation between measured and calculated weight loss for plug 17A is due to an extraordinary large grain loss for this plug caused by a missing filter in the core holder. However overall, the mass balance calculations indicate that the applied concept for estimating the reservoir conditions data is reliable.

Scenario 2 - CO₂-WAG Flooding

The reproducibility of the chemical data for Scenario 2 is similar to the reproducibility of data in Scenario 1 (Figures 4a and b). Again, the three distinct experimental phases with initial SW flooding, WAG flooding with CO_2 and SW, and SW flooding through the "dummy" plug can be discerned from the evolution in the measured water chemistry. As was also the case for Scenario 1, the batch calculations agree well with the measured dataset prior to flooding with CO_2 saturated water (step 1) and reasonably well with the measured chemical composition during flooding with CO_2 saturated water (step 3).

Figure 4a and b further illustrate that the estimated reservoir condition Ca-concentration and alkalinity (step 2) are much higher than measured and than calculated for Scenario 1. This is also what could be expected since the pore pressure is higher and the temperature lower as compared to Scenario 1. Thus, for Scenario 2 the estimated reservoir condition Ca-concentration is 4,370 mg/L compared to an average measured Ca-concentration of 2,300 mg/L. In line with this, the estimated alkalinity at reservoir conditions is nearly 200 mmol/L as compared to the measured alkalinity around 100 mmol/L in Scenario 2, and



the estimated pH at reservoir conditions is as low as 4.6 compared to the average measured pH of 6.1.

Figure 4 Modelling results (solid lines for step 1, 2, and 3) compared with measured chemical composition in the secondary sample cylinder during Scenario 2. **a**) Ca-concentrations (hatched lines are concentrations in SW and FW, respectively); and **b**) pH (numerical results blue) and alkalinity (numerical results orange).

The reliability of the estimated reservoir condition chemical state in the plugs was checked by calculating the expected amount of calcite to dissolve from the total volume of water flooded through the plug during the WAG flood and the estimated reservoir condition Ca-concentration of 4,370 mg/L. Using these values provide an estimated weight loss of 3.09 g for both plugs 19B and 22B. This estimate does not correspond equally well with the measured weight loss (2.60 g and 2.81 g for plugs 19B and 22B, respectively) as the case was in Scenario 1. There may be several reasons for this. One explanation could be that not all pore water is in contact with the residual CO_2 in the flooded plug during cycles with water flooding. This is the assumption in the numerical model, and therefore the model may overestimate the amount of calcite being dissolved. Another explanation could be that gypsum (CaSO₄) precipitation takes place in the plugs. If this is the case, the measured weight loss is underestimating the amount of calcite being dissolved. However, a porosity increase from 26.81% to 28.39% was observed for plug 19B as a result of the WAG flood. If we assume that the measured weight loss of plug 19B is due to calcite dissolution only, the corresponding estimated porosity after flooding will be 28%. Therefore, from an average point of view gypsum precipitation is unlikely in our case, but we can not reject that there may be a spatial trend in the dissolution/precipitation of minerals so that most calcite dissolution takes place in the inlet end of the plug while gypsum precipitation takes place in the downstream end. Some degree of gypsum precipitation would be in line with observations in other similar studies (Egermann et al. 2005; Madland et al. 2006).

In case the presented methodology was not applied we would estimate a weight loss of 1.44 g from the measured Ca-concentrations of approximately 2,300 mg/L. This deviates even more from the actual weight loss, and therefore we believe that the applied methodology provides reasonable estimates for the reservoir condition chemical state in

laboratory experiments and a good basis for subsequent regional scale chemical modeling. The methodology may be improved by the application of a true 2-phase numerical code such as TOUGHREACT (Xu et al. 2004) in a 2D or 3D model.

CONCLUSION

A novel sampling methodology for obtaining chemical samples and estimating reservoir conditions chemical composition of pore water in CO_2 flooding experiments has been developed. The presented sampling methodology and numerical concept is presently considered applicable only in the case where the hydrogeochemical system considered is mainly controlled by carbonate dissolution/precipitation in combination with CO_2 flooding. However, with few modifications, we believe that the concept can be utilized in experiments with more complicated hydrogeochemistry. Thus, the sampling methodology may be modified by determination of the gas composition in the sampling cylinder and precipitation and dissolution of other mineral phases may be incorporated in the numerical calculations.

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