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Comparison of OLI Studio: Analyser 9.2 and MultiScale™ Simulation Software for Design of MEG Regeneration Units

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Abstract

Mono-ethylene glycol (MEG) is a common thermodynamic hydrate inhibitor used in the production and transportation of oil and natural gas. MEG is usually recovered, regenerated in MEG regeneration and reclamation unit (MRU) and reused to minimize operation cost. However, systems containing MEG often contain high concentration of dissolved minerals and therefore may cause adverse scale. As scale is one of the biggest water-related problems, it needs to be predicted in advance to determine the best treatment strategy.

Simulation software are used to ensure efficient salt removal in the MRU, and therefore prevent scale. *Fjords Processing* currently uses MultiScale for the design of MRU. However, this simulation software cannot be integrated with a mass and energy simulation software as OLI Studio.

In this study, a comparison between OLI Studio and MultiScale™ software in the design of a MRU was done. Three sets of evaluations were made. The first set consisted of CO_2 partitioning calculations at different pressure, temperature, CO_2 concentration in the gas phase, alkalinity and MEG content. The second set was based on the reproduction of the experimental pH values measured by K. Sandengen in OLI Studio and in MultiScale™. These calculations were performed at 60 wt % MEG and 90 wt % MEG and at 25 ^{o}C and 80 ^{o}C. The third set of calculations consisted of a case study where typical MRU design calculations were made at different pressures, temperatures and MEG content.

The results showed that the difference between OLI Studio and MultiScale increased with the increasing content of MEG and decreased with the increasing temperature. CO_2 partitioning calculation showed a good correspondence between OLI Studio and MultiScale in the distribution of the species in water. For water-MEG solution, it was observed that OLI Studio predicted a slightly lower concentration of dissolved CO_2 than MultiScale. This corresponded with the pH calculations as well because OLI Studio predicted a slightly lower pH than MultiScale.

Case study calculations showed that pH difference between OLI Studio and MultiScale was higher than in other evaluations. This discrepancy must be due to difference between their scale prediction models. The difference between OLI Studio and MultiScale was insignificant for the calculations of the precipitation of $CaCO_3$ at the evaluated conditions. On the other hand, the calculations of precipitation of $Mg(OH)_2$ showed a notable difference between OLI Studio and MultiScale for solutions containing MEG.

Based on the significant difference in the prediction of the precipitation of $Mg(OH)_2$ and based on *Fjords Processing* experience in the design of MRU with MultiScale, the simulation software MultiScale seems to provide more reliable results than OLI Studio. Hence, further evaluation needs to be done before start using OLI Studio in the design of a MRU.

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Abbreviations and Symbols

AQ, aqueous thermodynamic model

IAP, Ion Activity Product

ΔG°, standard-state Gibbs free energy

ΔG, Gibbs free energy

R, gas constant

T, temperature

K, equilibrium constant

M, molality

MEG, Mono-Ethylene Glycol

MS, MultiScale

MSE, mixed solvent electrolyte thermodynamic model

MRU, MEG Regeneration Unit

MW, molecular weight

n, moles

OLI, OLI Studio: Analyser 9.2

pH, actual pH

P, pressure

ppm, parts per million

SR, Saturation Ratio

1 Introduction

Formation of hydrates and scales are considered one of the biggest water-related production problems in the petroleum industry. This solid material can build up and lead to blockage in of pipelines offshore and onshore. Beyond economic concerns, several industrial incidents, including serious injuries and fatalities are caused due to this formation [1, 2].

There is a number of approaches for preventing gas hydrates formation and deposition. Some of them include keeping the pressure and/or the temperature outside the hydrates zone, dehydration, modifying the gas phase with another gas phase and chemical treatment [2].

Among the chemical treatment, the thermodynamic hydrate inhibitors are by far the most common chemical class used to prevent hydrates formation. They are alcohols, glycols and salts [2].

Mono-ethylene glycol (MEG) is considered an important solvent which is often used in the oil and gas industry as a thermodynamic hydrate inhibitor during the production and transportation of hydrocarbons [3]. As high quantities of MEG are required to supress hydrates, recovery of MEG is necessary to minimize production cost [4].

In a MEG regeneration and reclamation unit (MRU), the original MEG is recovered through a regeneration process where a rich MEG (spent MEG with water or brine content grater that 25 wt %) is purified into lean MEG (MEG content higher than 90 wt %) [4]. Salts are also removed in the MRU to prevent increasing the ions concentration in the MEG loop [5].

In a MEG regeneration and reclamation unit (MRU), scale is commonly formed as a result of the minerals present in produced water mixed with MEG. These minerals form scale by exceeding their saturation limit due to fluctuations in operating temperature and pressure [4].

Prediction of scaling needs to be anticipated in advance to determine the best treatment strategy [2].

Scale removal can be expensive and sometimes impossible. Thus, prevention of scale formation is preferable to its treatment. In order to prevent scale formation, a thermodynamic method for prediction of scale formation potential can be used. Furthermore, thermodynamic model at specific temperature and pressure could be used to obtain supersaturation and scaling tendency of each salt in different brines. Recently, many researches have been focused on this area and therefore several scale prediction models have been presented [6].

OLI Studio and MultiScale™ are popular simulations software used for electrolyte chemistry and scale prediction. While MultiScale™ is developed specifically for prediction of mineral solubility in the presence of MEG [7], OLI Studio is develop for prediction of mineral solubility of a wider range of solutions, including mixed organic-water solvents up to saturation [8].

The use of OLI Studio and MultiScale™ software to simulate the chemistry in a MRU has been beneficial to oil service companies to predict the conditions at which scale is formed and provide a good design. Nevertheless, as both software are designed differently, identifying the difference between them is important to prevent designing errors.

1.1 Objectives of this Work

This thesis is performed in cooperation with *Fjords Processing*. Currently, *Fjords Processing* uses MultiScale™ for computing the chemistry in the MRU. Comparison and identification of the differences between OLI Studio and MultiScale™ will facilitate *Fjords Processing* to foreseen the difference between using OLI Studio and MultiScale when designing a MRU. In addition, OLI Studio software capabilities seem to be more extended compared to MultiScale™.

One of the advantages of the OLI Studio for *Fjords Processing* can be capability to be integrated with a mass and energy balance simulation software to simulate the MRU. This integration allows *Fjords Processing* to perform process modelling and analysis of aqueous electrolyte systems quicker and reliable.

The objective of this research is to perform typical MRU design calculation with OLI Studio and with MultiScale™ in order to evaluate and compare the performance of the two electrolyte chemistry software, used for scale prediction.

Design calculations performed with MultiScale™ will be done at Fjords Processing while Design calculations performed with OLI Studio will be done at the University of Stavanger. Evaluation of the results is to be discussed with the personal at *Fjords Processing*.

1.2 Novelty of the Research

Currently *Fjords Processing* uses MultiScale™, and this simulation software cannot be integrated with a mass and energy balance simulation software unlike OLI Studio. But before start using OLI, it is important to identify the difference between OLI and MultiScale. Identification and evaluation will prevent design inaccuracies and therefore increasingly stringent environmental regulations.

1.3 Company Overview

Fjords Processing provides wellstream processing technology, systems and services to the upstream oil and gas industry. *Fjords Processing* has a wide experience with design and operation of MRU. It offers different design configurations pending on the specific field requirements [9].

1.4 Thesis Outline

The second chapter presents relevant theory to increase readability and to identify noticeable differences between the two electrolyte chemistry models of on which the software are based. The third chapter considers the procedure how the calculations were developed. Important assumptions and model input data are presented in this chapter.

The chapter four provides the results and discussions for the calculations performed using both software. The calculations consist of pH determination in a water–MEG-CO_2 solution at different concentrations of $NaHCO_3$, CO_2 partitioning in water-MEG solutions at different conditions and a study case which covers the determination of the pH, concentration of Ca^{2+}, and Mg^{2+} of a rich MEG solution as function of the alkalinity added. The results are evaluated and interpreted according to the thesis objectives. The final chapters of the thesis are conclusions and recommendations, where main outcomes of the research presented together with further research.

All the detailed data for results can be found in Appendices in the end of the thesis.

2 Theory

This chapter presents the scale and hydrates formation problems in the oil and gas industry. Also, overview of the scale prediction software OLI Studio and MultiScale™ is provided, together with the most important principles regarding scale formation and description of the MEG regeneration unit.

2.1 Scale Formation Problem in the Oil and Gas Industry

Scale is defined as the deposition of soluble inorganic salts, metal carboxylates or metal naphthenates from aqueous solutions [2]. It is formed when the solution contains more dissolved ions than is thermodynamically possible, in other words, when the solution is supersaturated. Changes of the process conditions or composition of the stream can lead to supersaturation [7].

Scale deposition can occur on any surface, Figure 2-1 shows scale deposition inside a pipeline. Once a first scale layer is formed, it will continue to grow unless treated. In petroleum industries, scale can occur anywhere along the production conduit, from the equipment in the well to the equipment in the processing facilities [2].

Figure 2-1: Scale built up in plumbing pipes [10]

Saturation tendency (ST), also called supersaturation ratio, is defined as the ratio of the IAP (Ion Activity Product) to the thermodynamic limit based on the thermodynamic equilibrium constant. If ST<1, then the solid is under-saturated, if ST>1, the solid is super-saturated and if SR=1, the solid is at saturation/equilibrium [11].

The most common types of scale encountered in the oil industry in order of prevalence are calcium carbonate, sulphate salts, sulphide scales and sodium chloride [2].

Salts can be classified depending on their solubility. For most salts, solubility increases as temperature increases. These salts are commonly called high solubility salts. On the other hand, low solubility salts belong to those salts which solubility decreases with increasing temperature [2]. Figure 2-2 shows an example of the solubility tendency as function of the temperature for two high solubility salts (sodium chloride and potassium chloride) and two low solubility salts (calcium carbonate and calcium sulphate). The data in Figure 2-2 is obtained from calculation performed with the OLI Studio simulation software [12].

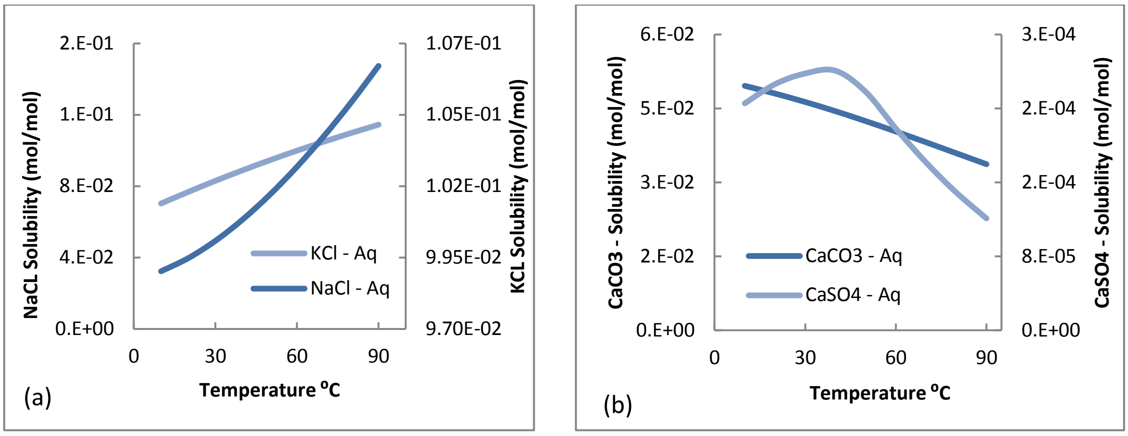

Figure 2-2: (a) Sodium chloride and potassium chloride solubility as function of the temperature. (b) Calcium carbonate and calcium sulphate as function of the temperature [12].

2.2 Scale Prediction Models

Scale prediction models are important tools that are typically used to foresee scale risks during production, on green fields under development or to understand the cause of scaling ion producing existing fields.

Several commercial scale prediction models have been developed for modelling production processes reasonably closely and with the use of the best thermodynamic data obtained from both theoretical and laboratory sources [13].

Some of the most used tools for scale prediction are OLI Studio, MultiScale™, Scale200 and ScaleSoftPitzer. In this thesis we focus on OLI Studio and MultiScale™.

In the following section, MultiScale™ and OLI Studio simulation software are described.

2.2.1 Multiscale™

MultiScale™ simulation software has been in the market since 1993 and it is owned by Statoil, but Expro Fluids has been licensed to sell and further develop the program [14].

It is continuously upgraded with new features and data when made available. By 2006 MultiScale™ has extended its model to include the possibility for predictions in MEG containing solutions. This work has been carried out by Kristian Sandengen at the Department of Materials Science at the Norwegian University of Science and Technology, and at the STATOIL research centre at Rotvoll, Trondheim [7].

Chemistry models

As stated in the work of K. Sandengen, experimental solubility data and thermodynamic data taken from literature were utilized to construct empirical functions for the influence of MEG on mineral scale formation. The aqueous model combines an equation of state (gas+oil phase) with the Pitzer ion interaction model (water phase) to describe the multiphase behaviour of gas-oil water systems [7].

When MEG is introduced into the water phase model, the activity of a specie (i) is given as its concentration *(*m) times the activity coefficient (ϒ), which is divided into two parts: Υ^S, which takes care of the “salt effect”, and Υ^N, which takes care of the “MEG effect”. This is represented in Equation 1 [7].

$$a_i = m_i \Upsilon_i = m_i \Upsilon_i^S \Upsilon_i^N$$

Equation 1 Activity of a specie

The Υ^N is empirically fitted from solubility data and dependent on MEG concentration. In addition, for some systems with high ionic strength, it is a function of both temperature and ionic strength in addition to MEG concentration. The Υ^S is calculated as the solvent is water and therefore do not depend on MEG concentration [7].

The MultiScale™ model has a “MEG calculation routine” to calculate new equilibrium constants and activities. Then the model calculates the whole multiphase equilibrium as if the solvent was water. MEG activity is only used for calculation of partial pressure that is used in the Pressure Volume Temperature part of the model [7].

Range of applicability

- This model is valid up to approximately 99 wt % MEG [7]
- Functions providing MEG dependence have been fitted from data in the 0-100^{o}C, using the model outside this range (temperatures higher than 120^{o}C) will give uncertainties [7]
- The model is not suited for calculations where the temperature is high, and/or several highly soluble species like Na^+, K^+, CO_3^{2-}, Cl^-, etc. are present yielding a high salinity (higher than 1 mol/kg)[7]
- Mixing up to 6 waters, 6 oils and 6 gases simultaneously [14]
- This model predicts the water chemistry and the scaling tendency of the following minerals: NaCl, KCl, $BaSO_4$, $SrSO_4$, $CaSO_4$, FeS, $CaCO_3$, $FeCO_3$, $BaCO_3$, $SrCO_3$, $NaHCO_3$, $KHCO_3$, Na_2CO_3, K_2CO_3, NaAc, $Mg(OH)_2$, $MgCO_3$ [14]

2.2.2 OLI Studio

Dr. Marshall Rafal founded OLI Systems in 1971 and during the past four decades OLI has developed commercial computer software, OLI Studio [8].

Starting in 2000, OLI Systems with extensive support of the US Government, in the form of four major awards for sponsored research, has extended its predictive capabilities to encompass mixed solvent electrolyte systems [15].

By 2013, OLI Systems developed a comprehensive thermodynamic model for calculating thermodynamic and transport properties of mixtures containing MEG, water, inorganic salts and gases. The comprehensive thermodynamic model was based on a combination of the MSE model and the extensive thermodynamic data that was available in the literature for MEG-containing systems[15].

OLI Engine is also available through major process flowsheet simulations as Unisim, Aspen Plus, HYSYS, PROII, gPROMS, and IDEAS [15].

Chemistry models

OLI Studio simulation software uses a model based on the work developed by Debye and Huckel, Helgeson, Pitzer, Meissner, and others. The OLI electrolyte approach is based on a theoretical framework and data regression methods [16].

The predictive framework is based on the revised Helgeson equation of state for predicting the standard state of thermodynamic properties of all species. The modern formulations included in the OLI framework are:

I. Bromley-Meissner (semi-correlative) which can predict and extrapolate excess properties when data is limited or unavailable,
II. Pitzer (highly Interpolative) for verifying the standard state model employed, Helgeson and the mixed solvent electrolyte (OLI’s New Framework), see Table A-1 in the Appendix A [8].

The development of the thermodynamic models for mixed-solvent electrolyte (MSE) systems contains several contributions that define the excess Gibbs energy. The contributions include:

- Long-range force for electrostatic interaction between ions, generally presented by Debye-Hückel equation
- Short-range interaction which includes the interaction between species
- The Born model which represents the electrostatic contribution to ion solvation

An expression for the excess Gibbs energy G^{ex} is constructed as a sum of three terms, G^{ex}_{LR} represents the contribution of long-range electrostatic interactions, G^{ex}_{MR} is the short-range interaction contribution and an additional (middle-range) term: G^{ex}_{SR} accounts for ionic interactions that are not included in the long-range term, R is the gas constant and T is the temperature, see Equation 2 [17].

$$\frac{G^{ex}}{RT} = \frac{G^{ex}_{LR}}{RT} + \frac{G^{ex}_{MR}}{RT} + \frac{G^{ex}_{SR}}{RT}$$

Equation 2 Excess Gibbs energy expression

The MSE model has removed both concentration limit and the presence of water as limits to its simulation capability. The MSE model is recommended and preferred when the chemistry of interest contains significant amounts of highly miscible components such as HF, MEG, methanol, etc. [17]

Range of applicability of the MSE model

- The mole fraction of the species concentration in the liquid phase resulting from the equilibrium calculations is between 0 and 1.0 [18]

- The temperature resulting from the equilibrium calculations must fall in the range between 0 °C and 1200 °C [18]

- The pressure resulting from the equilibrium calculations must fall in the range between 0 bar to 1500 bar[16]
- Full data bank, covers thousands of species in water and organic chemical compounds. Moreover, OLI allows users to provide their own supplementary databanks [16]
- No limit for ionic strength [19]

2.3 Aqueous Chemistry

The following section presents the fundamentals of aqueous chemistry related to the scale prediction models.

2.3.1 Chemical Equilibrium

Chemical equilibrium is defined as the state in which the concentration of all reactants and products are constant over time. Identification of key variables relevant in determining water-mineral relations and water and atmosphere relations is typically done by the chemical equilibrium model. Molar Gibbs free energy describes the direction and extent of a processes approaching equilibrium [20].

For example, the standard-state free energy (ΔG°) of the dissolution of calcite in reaction (1) is negative. This means that the dissolution of calcite proceeds spontaneously if H^+, Ca^+, and HCO_3^- are all present at unit activity (i.e., 1mol/L).

$$CaCO_{3(s)} + H^+ \leftrightarrow Ca^+ + HCO_3^- \tag{1}$$

An important statement that provides a direct relationship between a fundamental thermodynamic quantity, the free energy of reaction, and the equilibrium constant for reaction are given in the Equation 3 [21].

$$\Delta G^{\circ} = -RT\ln K$$

Equation 3: Free energy of reaction

Where;

ΔG°, is the standard-state free energy, kj/mol
R, is the gas constant, J/molK
T, is the temperature, K
K, is the equilibrium constant [21].

Discrepancies between predicted equilibrium composition and the actual data of the system can provide valuable understanding of those cases in which non-equilibrium conditions prevail, or where analytical data for the system are not sufficient accurate or specific. Such divergences are incentive for research and improvement of existing models [20]. Equation 4 can be used for calculating K.

$$K=([C]^{C}[D]^{d})/([A]^{a}[B]^{b})$$

Equation 4: Equilibrium constant equation

Where,
[A], [B], [C] and [D], represent equilibrium molal, and,
a, b, c and c are the molar amounts of compounds A, B C and D respectively.

LeChâtelier's Principle provides a general understanding the behaviour of a system when subjected to external force or stress. It states that for a system in equilibrium, external changes will be accompanied by changes in the state of the system which will react to reduce the magnitude of the initial change. The changes involved include changes in concentration, pressure or temperature [22].

For example, a reaction in equilibrium will shift to the right when the concentration of the reactants is increase. In the same way, it will shift to the left when the concentration of the product is increased. Increasing the pressure will shift the reaction in equilibrium to the side of the equation that has fewer gas-phase species [23].

2.3.2 Solubility Product and Saturation

The Gibbs free energy (ΔG) of the dissolution is a good indicator of its saturation state. For spontaneous reaction, ΔG is negative. For ΔG higher that 0, the reverse reaction is spontaneous. For systems in equilibrium, ΔG is cero [24].

The actual ion activity product (IAP), product of specific ions, may be compared with K and if the IAP is higher than the K the solution is oversaturated, if the IAP is equal to K the solution is saturated (equilibrium) and if the IAP is lower than the K, the solution is undersaturated (Equation 5) [20].

$$IAP=([C]^{C}[D]^{d})/([A]^{a}[B]^{b})$$

Equation 5 IAP equation

Where,
[A], [B], [C] and [D], represent the actual molar concentration,
a, b, c and d are the molar amounts of compounds A, B C and D respectively.

2.3.3 Aqueous Speciation of CO_2

The physical equilibria for CO_2 dissolved in water is given by the reaction (2), while the chemical equilibria is given in reaction (3) and (4) which define the acid-base chemistry of aqueous CO_2. Reaction (3) and (4) are related to the physical reaction (2) as stated by Henry's law. Figure 2-3 shows the speciation of CO_2 in water as function of pH [25]. In addition, as described by Henry's law, the solubility of the dissolved CO_2 is depended on its partial pressure [26].

$$CO_{2\,(g)} \leftrightarrow CO_{2\,(aq)} \tag{2}$$

$$CO_{2\,(aq)} \leftrightarrow H^{+} + HCO_3^{-} \tag{3}$$

$$HCO_3^{-} \leftrightarrow H^{+} + CO_3^{2-} \tag{4}$$

Carbon dioxide is slightly soluble in pure water and as with all gases, the solubility decreases with temperature [27]. Also The equilibrium constant of the reaction (3) is higher than the equilibrium constant of the reaction (4) [28].

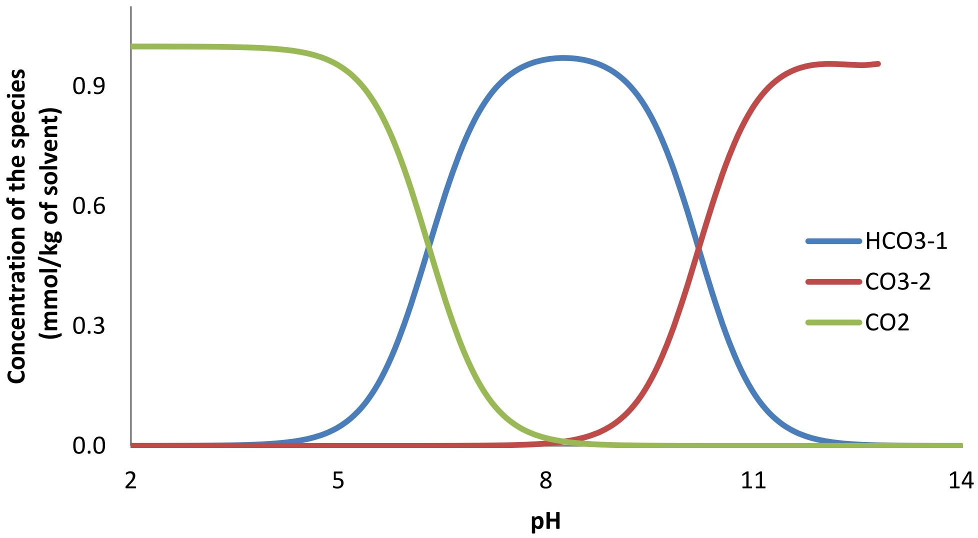

Figure 2-3: Speciation of CO2 in water as function of pH [12]

2.3.4 Alkalinity

Alkalinity is a measure of the water's ability to neutralize an acid, in other words, alkalinity acts like a buffer, which prevents fluctuations of the pH [29]. It is defined as the sum of the bicarbonate, carbonate and hydroxyl ions concentration minus the hydrogen ion concentration [30]. This relationship is shown in the Equation 6 [31]. Alkalinity is used to describe composition, buffer capacity and pH behaviour of waters in many different fields of science [32].

$$\text{Total Alkalinity} = HCO_3^{-} + 2CO_3^{-2} + OH^{-} - H^{+}$$

Equation 6 Total alkalinity calculations [31]

In acidic systems, the CO_3^{-2} can be safely neglected because, as it is shown Figure 2-3, the CO_3^{-2} is not dominant specie [33].

2.4 Mono-Ethylene Glycol

This section describes the properties of the hydrate inhibitor Mono-ethylene glycol (commonly denoted as EG or MEG), a typical MEG regeneration unit and pH determination in mixed solvents.

2.4.1 MEG as Hydrate Inhibitor

Gas hydrates are ice-like clathrate solid that are formed from water and light hydrocarbons at elevated pressure and lower temperature. They are most frequently encountered in subsea or cold climate wet gas or multiphase pipelines [2].

Gas hydrates can block the flow of fluids in pipelines, as shown on Figure 2-4. They can be formed during drilling, completion, and workover operations. It can occur in gas-processing facilities, gas and water injection lines and aqueous chemical injection in gas lift lines if the pressure-temperature conditions are met [2].

There are several methods used for preventing gas hydrates. These methods include, controlling pressure and temperature to outside the hydrate zone, dehydration, modification of the gas phase, and addition of chemical [2].

Figure 2-4 Gas methane hydrate recovered in core catcher during bottom sampling aboard USCGC Healy in the Southern Beaufort Sea in 2010 [34].

Thermodynamic inhibitors are the most popular chemicals used to prevent hydrates. It includes methanol and MEG [35].

MEG physical properties are shown in Table 2-1. Glycol is the most widely used, due to its availability and cost. It is used as gas inhibitor, as antifreeze in automobile cooling systems and in the manufacture of human-made fibre, low freezing explosive, among other uses. Glycol is nearly colourless and slightly viscous liquid [36].

MEG is considered environmentally friendly as biodegradation studies show MEG with 97 % biodegradation after 20 days, it is classified as a green additive by the Climate and Pollution Agency. Nevertheless, it is HSE-classified as red [37, 38].

Table 2-1 Mono-ethylene glycol physical properties [39]

Physical Property	**Value**
Chemical formula	$C_2H_6O_2$
Boiling point, ^0C	197.5 ^{0}Cat 1 atm
Density, kg/m3	116
Molecular weight, g/mol	62.068

MEG works as hydrate inhibitor due to its capacity to compete for the water hydrogen bonding with itself, making it harder to form hydrates compared to when no inhibitor is present. The forces between water and MEG have been experimentally determined to be 10 times higher than normal van der Waals forces between uncharged molecules. Addition of MEG prevents the water molecules from contributing in the solid hydrate structure, and keeps the water in liquid phase. The more MEG is added to the system, the more water is prevented from participation of hydrate formation, as higher pressure and lower temperatures are required for formation of hydrates from the remaining, uninhibited water [40]. Figure 2-5 shows the effect of MEG content in hydrate inhibition. MEG is added at very high concentrations, for instance, up to two barrels of MEG can be added per barrel of water in the production pipeline, this necessitates the recovery of the original MEG through regeneration process [2].

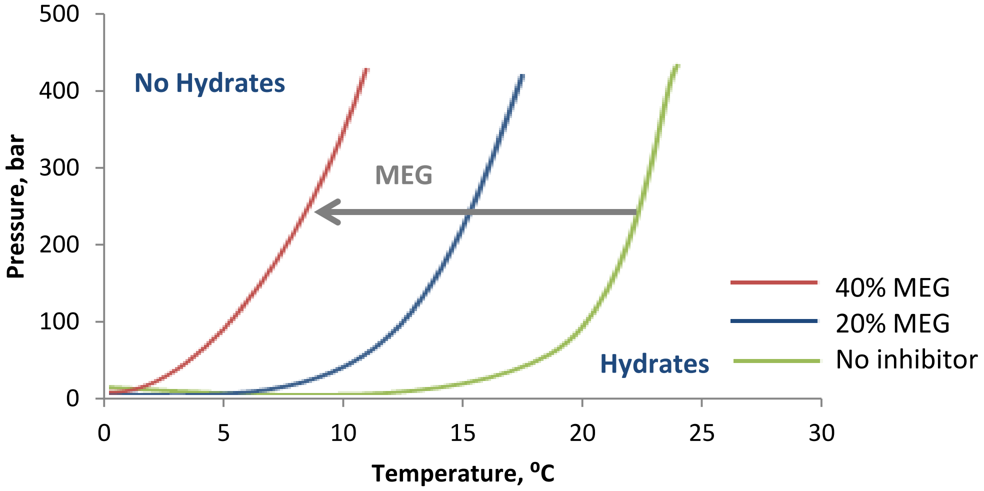

Figure 2-5: Effect of MEG % in hydrate inhibition [41]

2.4.1 MEG Regeneration Unit

Due to the high amount of MEG required to prevent hydrates, it is necessary to recover the original MEG through a regeneration process. After its regeneration, MEG is recycled to reduce cost [4].

The MRU typically contains two storage tanks (see Figure 2-6), one for rich MEG and one for lean MEG. The purpose of the storage tanks is to allow maintenance and for contingency. In addition, the rich MEG storage tank plays and important role in the design of the MRU because it provides an indication of the concentration of the CO_2 dissolved in the feed. This information is required for calculation of the alkalinity required to remove the salts from the rich MEG [42].

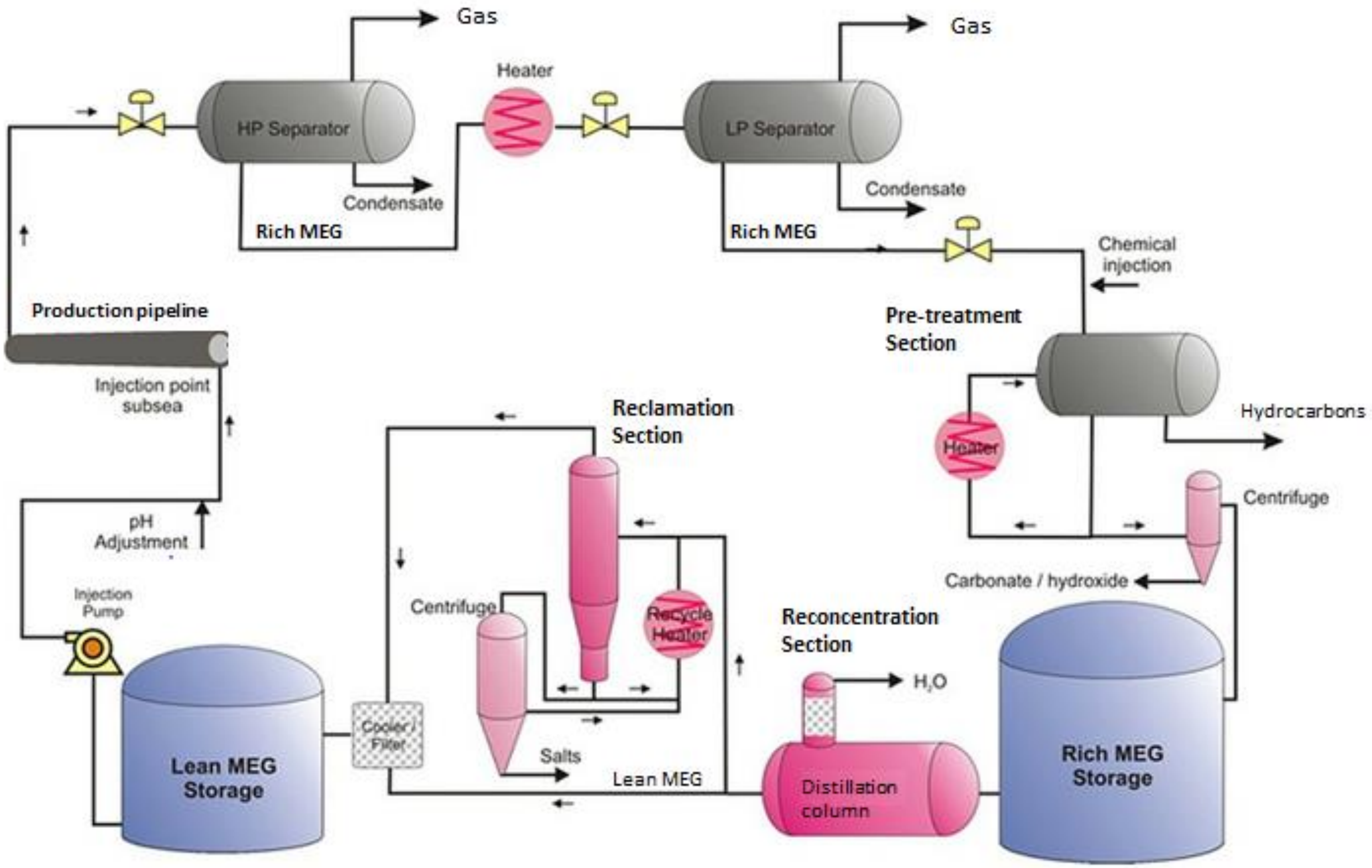

Figure 2-6 Typical MEG loop [43]

Rich MEG that enters the regeneration process typically contains 45-60 wt % MEG. It contains some dissolved gas and hydrocarbons, passes through a 3-phase separator vessel where the gas is flashed off and liquid hydrocarbons are sent to the condensate recovery system. The rich MEG is sent either to storage or directly to the dowstream systems [44]. It also contains dissolved salts needed to be removed before re-used to prevent scale formation in the downstream equipment. The regenerated water-MEG solution has a concentration of approx. 90 wt. % MEG , called lean MEG [4].

The system where the MEG is regenerated, the MRU, typically consist of pre-treatment section, reconcentration section and reclamation section [4].

The purpose of the pre-treatment section is to remove all divalent cations (Ca^{+2}, Mg^{+2}, Sr^{+2},Fe^{+2}) from the rich MEG by precipitating them as carbonate and hydroxide salts. This typically is done by raising the pH to 9.6 and increasing the temperature to 80 ^{o}C[4]. The rich MEG, which contains some dissolved gas and hydrocarbons, passes through a 3-phase separator vessel where the gas is flashed off and liquid hydrocarbons are sent to the condensate recovery system. The rich MEG is sent either to storage or directly to the downstream process [44].

The purpose of the reconcentration section is to remove water from the rich MEG solution. This process is typically done in a distillation column at ambient pressure and 120˚C. The regenerated MEG is taken from the bottom of the distillation column and typically contains 80-90- wt % MEG [4].

High solubility salts (KCl, NaCl) and other contaminants are removed in the reclamation section by evaporation under vacuum and temperature from 120 to 150˚C [45]. The salts formed in the pre-treatment and reclamation section are typically removed using centrifuges [4].

MEG MRU design is unique, the design depends on the rich MEG physical properties, projected volumes, and desired quality of lean MEG [46].

A typical MEG-loop is shown in Figure 2-6, where the rich MEG comes with the production pipelines, is separated out in the high pressure separator and low pressure separator and then it enters the MRU where it is regenerated so it can be reinjected into the production pipeline [43].

2.4.2 pH measurement for MEG-water mixtures

The pH is one of the key parameters measured in the MEG regeneration units to control quality and meet specification [47].

Its measurement has been one of the most complex establishments of standards in quality control. Its complexity is linked to environment considerations and the solvent type. The results, as specified in IUPAC recommendation, are distinct pH scales for each solvent linked to one reference value standard plus a group of primary standards and operational standards. Nevertheless, the availability of such standards is limited to a few nonaqueous solvents or aqueous-organic solvent mixtures, including MEG mixtures [47].

There are several publications related to calibration, measurements and interpretation of pH in mixed solvents as MEG/water [7]. One of the methods used for pH measurement in MEG/water mixtures is describe by Mussini et. al. (1991), where the reference standard value is based on the electromotive force measurements of the cell Pt|H_2|RVS Buffer + KCL|AgCl|Ag|Pt over a range of temperatures and solvent compositions [47].

The simulation software OLI Studio and MultiScale™ calculate the pH using different methods, which are described below. Therefore discrepancies between their calculated pH can be expected.

MultiScale™

To verify the pH in the MultiScale™ prediction model, K. Sandengen proposes to measure the pH in a water-MEG solution based on calibration values given by Mussini et. al., and the calibration method of water+methanol mixtures described by Kan.et.al. He states that there are two important sources for determination of pH in MEG-water mixtures; salinity and MEG content. This solution chemistry affects the outer potential, which give rise to the pH, see Equation 7.

$$pH = pH_{meas} + \Delta pH_{Salt} + \Delta pH_{MEG}$$

Equation 7 pH determination in water-MEG solutions

Where;
pH, the actual pH
pH_{meas}, the water based pH
ΔpH_{Salt}, the pH contribution due to the salt content in the mixture
ΔpH_{MEG}, the pH contribution due to the MEG content.

ΔpH_{MEG} was calculated based on a ΔpH_{MEG} function of MEG weight fraction and temperature. The function to be used is depended on the electrodes used and the temperature at which the measurement was done.

The ΔpH_{Salt} was only necessary to quantify when the solution ionic strength, I>>0.1. ΔpH_{Salt} was calculated based on a ΔpH_{Salt} function of ionic strength and it was independent on the MEG content.

After comparing the data from MultiScale™ with the experimental data, K. Sandengen concluded that the model and the results corresponded well, the exception was at 80 ^{o}C in 90 wt % MEG, where the model gives a too high pH at high contents of $NaHCO_3$. K. Sandengen explained that the discrepancies may be due to measuring difficulties, as the different pH electrodes show much larger individual variation and drift at high temperature. He also mentioned noted that the model is fitted using data from measurements with only about 10mmol/kg of $NaHCO_3$ and that variations can be observed at higher concentrations [7, 48].

OLI Studio

As the MSE model predicts the Gibbs energies of transfer of electrolytes on the basis of data such as solubility, a prediction of single-ion properties such as pH, requires extra-thermodynamic assumptions and has to depend on the adopted reference state (i.e., a pH scale) [42]. Consequently, The OLI Studio reported pH is computed from the H_3O^+ activity and does not include the $HOC_2H_4OH_2^+$ activity (protonated glycol molecule). That is, the computed Aqueous pH is based on the protonated water solvent and not a mixed-solvent (H_3O^+ + $MEGH^{2+}$) [3, 49, 50].

As pH does not agree quantitatively with experimental data in solvents that are dominated by glycols, OLI Systems proposed a practical approach based on the concentration-based definition of pH (Equation 8) [42].

$$pH=-Log(c_H)$$

Equation 8 pH determination based on concentration [42]

Where;
c_H is the molar concentration of the protonated solvent.

In MEG solutions, the protonated specie $HOC_2H_4OH_2^+$ is present because of the self-dissociation of MEG as shown by reaction (5)

$$2HOC_2H_4OH_{(aq)}= HOC_2H_4OH_2^{+}+ HOC_2H_4OH^{-} \qquad (5)$$

Thus, in water-MEG solutions, the pH can be calculated as shown in Equation 9. Both protonated solvent species (H_3O^+ and $HOC_2H_4OH_2^+$) contribute to the solution pH. The self-dissociation constant of MEG has been assumed to have a similar temperature dependence as that of water [42].

$$pH\approx-Log(c_{H3O+}+c_{HOC2H4OH2+})$$

Equation 9 pH determination in water-MEG solutions based on concentration [42]

2.5 Multiscale™ and OLI Studio Input Format Limitations and Flexibilities

Before performing typical calculations for the MRU design in OLI Studio and MultiScale™, it is valuable to look at their input format limitations and flexibilities. This chapter describes the input format in MultiScale™ and in OLI Studio for the calculations performed in this research.

2.5.1 Input Format in Multiscale™

Single stream tool in MultiScale™ is used for the typical calculations performed in this research. Single stream calculation input is divided into four sections:

- Water Analysis
- Oil Analysis
- Gas Analysis
- Tune Analysis

From the sections above, Water Analysis and Gas Analysis are normally used for describing the input stream in MultiScale™.

Water analysis input is sub-divided into the following sections:

- Water information, for providing the name and add information about the stream
- Analysis conditions, to set the pressure, temperature and the gas-water ratio
- Ion concentration, to set the concentration of the total alkalinity and the concentration of Na^+, K^+, Mg^{2+}, Ca^+, Ba^{2+}, Sr^{2+}, Fe^{2+}, Cl^-, Br^- and SO_4^{2-}
- Select model, to select one of the following options as input:

        - Composition of equilibrium gas (CO_2, H_2S and CH_4)
        - pH
        - Concentration of gas (CO_2, H_2S and CH_4) in aqueous phase
        - No gas in phase
    - Organic acids, to set the concentration of methanoic acid, acetic acid, propanoic acid and botanic acid
    - Enter MEG concentration and unit, to set the MEG concentration and select if the value is relative to water or to the solution
    - Density, to enter the density if preferable, otherwise, the program can make an estimate
    - H_2S scavenger, to set the scavenger concentration

Gas analysis input is sub-divided into the following sections:

- Fluid information, for providing the name and add information about the stream
- Fluid tuning, to select whether adjusting to saturation point is required.
- Fluid type and, data, to introduce the concentration of MEG, H_2O, N_2, CO_2, H_2S, C1, C2, C3, iC4, nC4, iC5, C6, C7, C8, C9 and C10.

The input unit for the species concentration available in MultiScale™ are mg/l, mmol/l, mg/kgH_2O, mmol/kgH_2O, mg/kgSolvent and mmol/kgSolvent.

2.5.2 Input Format in OLI Studio

The tools used for input data in this research are:

- Stream, used when the data is expressed as molecular concentration, and
- Water analysis, used when the data is expressed ion concentration.

Stream input consists of:

- Description, for providing the date, the name and additional information about the stream
- Definition, to set the input data, this section is divided into:
    - Stream Parameters, where the stream amount, the temperature and the pressures is added
    - Inflows, where only molecular concentrations can be added,
    - Chemistry model, to select between, AQ model or MSE model
    - Add calculation, to select from the calculations below:
        - Single point
        - Survey by temperature, pressure, composition, pH, vapour factor and vapour amount
        - Chemical diagram
        - Stability diagram and,
        - Corrosion rates

From the calculations above, single point calculation and survey calculation by temperature and pressure were used in this research.

The water analysis input consists of:

- Description, for providing the date, the name and additional information about the stream
- Analysis, to set the input data, this section is divided into:
  - Analysis Parameters, where the stream amount, the temperature and the pressures is added
  - Recorded properties, where the total dissolved solids, measured pH, measured alkalinity, density and specific electrical conductivity can be added.
  - Neutrals, where molecular concentrations can be added
  - Cations, for cations concentration
  - Anions, for anions concentration
  - Chemistry model, to select between, AQ model or MSE model
  - Add reconciliation, to select from the calculation below:
    - No reconcile
    - Reconcile pH
    - Reconcile pH/alkalinity

No reconcile calculation was used on this research. Once the water analysis calculation is made it can be copied to a stream to perform survey calculations.

The internal calculations in OLI are performed in SI units, but data can be entered as SI, Metric, English, etc.

2.6 Comparison between OLI Studio and Multiscale™

Based on the theory above the main differences identified are shown in the Figure 2-7.

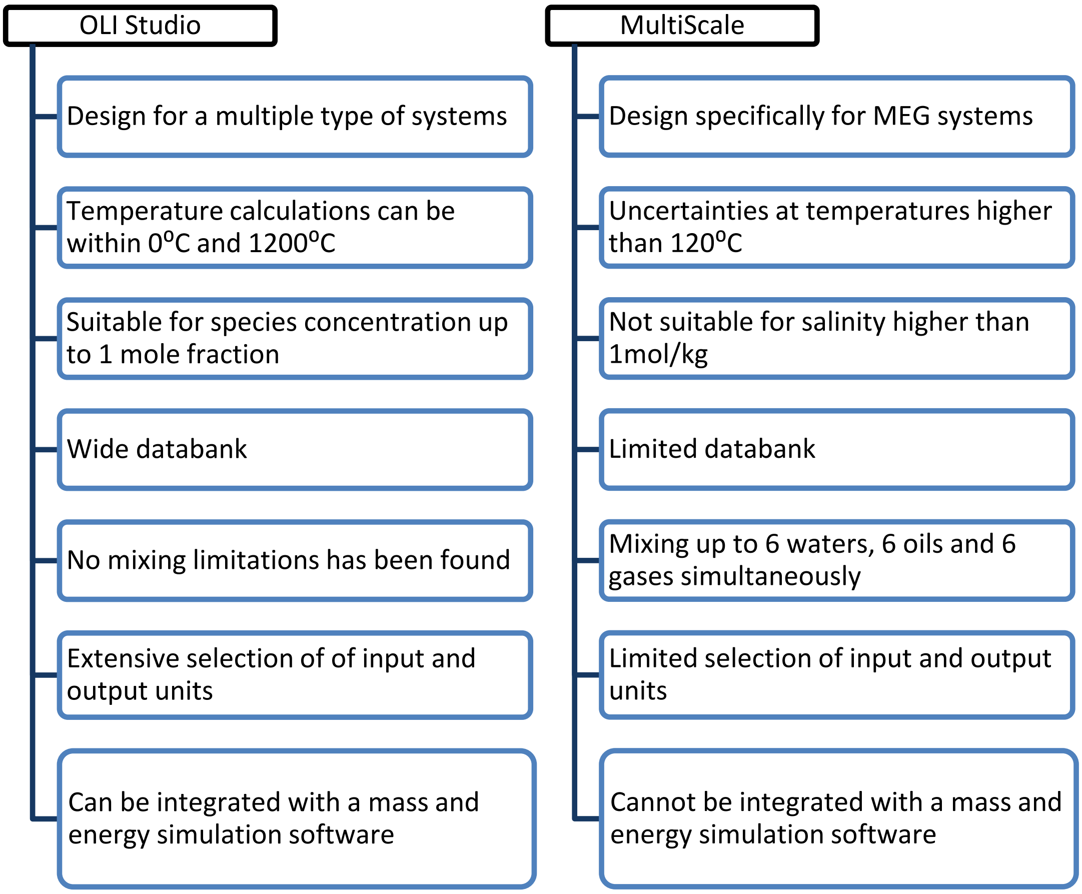

Figure 2-7: Schematic representation of the main difference between the two chemistry model, MultiScale™ and OLI Studio

It can be concluded from this section that as shown Figure 2-7, there are notable difference between OLI Studio and MultiScale™. Experimental comparison between these software will be evaluated in the following sections.

3 Experiment Description - Process Simulations

The purpose of performing these calculations was to identify differences between OLI Studio and MultiScale™ in terms of parameters that affect the design of a MRU. This chapter describes the materials, methods and input data applied when building the simulation model.

3.1 Materials

The following software were used:

- OLI Studio 9.2.8: USB based educational license.
- MultiScale™: USB based license.

OLI Studio 9.2.8 license was obtained from the University of Stavanger while MultiScale™ was obtained from *Fjords Processing*.

For simplicity, OLI Studio 9.2.8: Stream Analyser will be referred as OLI Studio in the text and OLI in the graphs, MultiScale™ will be refer as MultiScale in the text and MS in the graphs.

3.2 Methods - Simulation model

The simulations consisted of:

1) CO_2 partitioning variating pressures, temperatures, alkalinities, $CO_{2(gas)}$ concentrations and MEG concentrations,

2) pH determination at different temperatures and MEG concentration and,

3) A case study, where typical parameters when designing the pre-treatment section of the MRU are evaluated at different pressures, temperatures and MEG concentrations.

Figure 3-1 shows a schematic overview of the simulations performed.

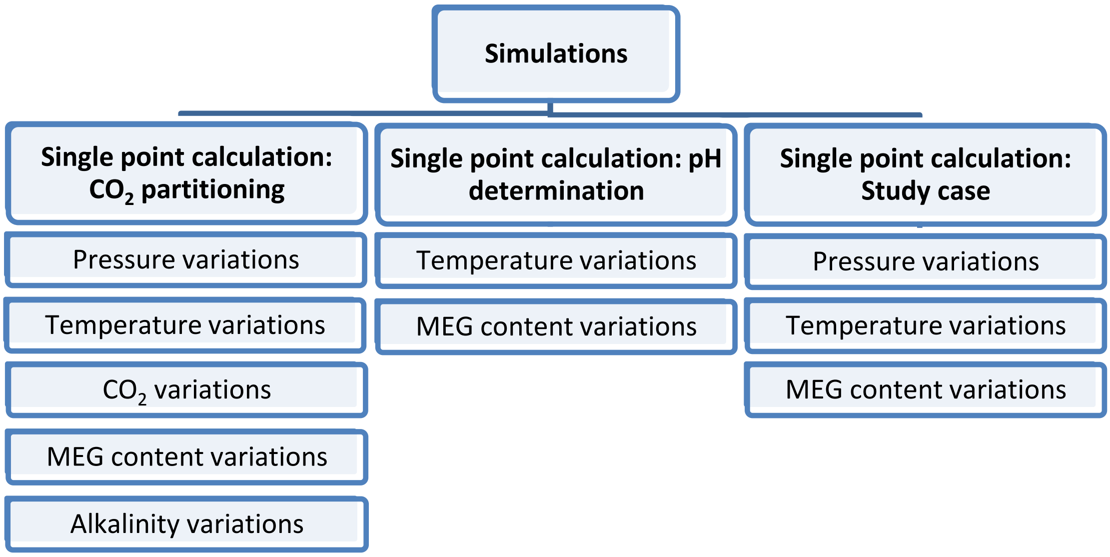

Figure 3-1 Schematic overview of the simulations performed

3.2.1 CO_2 Partitioning

The aim of this calculation is to evaluate the speciation of the CO_2 at different conditions. This evaluation is typically performed in the Rich MEG storage tank to foresee the CO_2 dissolved in the feed. This evaluation is important for calculating the alkalinity dosing required to remove the low solubility salts in the pre-treatment section.

OLI Studio and MultiScale were used for CO_2 partitioning for solutions with and without alkalinity and at the conditions mentioned in the Table 3-1. The input data is based on the calculations performed in MultiScale provided by *Fjords Processing*.

Table 3-1: Conditions evaluated for CO_2 partitioning calculations

Pressure range, Bar	1 - 10
Temperature range, ^{0}C	1 - 100
wt % MEG	0, 10 and 50
mol % CO_2 in vapour	0.1, 1 and 10
Alkalinity, mmol/kg	0 and 5

The CO_2 partitioning calculations in MultiScale were performed by *Fjords Processing* and the calculations with OLI Studio were then performed as stated in the following section, using the same input.

Calculations set up OLI Studio

As the input format in OLI Studio and in MultiScale varies, some additional calculation steps were done.

The Aqueous model (AQ) was used for the calculations performed at 0 wt % MEG while the Mixed Solvent Electrolyte model (MSE) was used for the calculations with solutions containing MEG.

The calculations steps were performed in the following manner:

a. Two input streams were made; one for the liquid phase and the other one for the gas phase. The input data in OLI Studio is shown in Table 3-2.
b. The streams were combined using a tool from OLI Studio called mixer,
c. The results from the mixer were copied to a new stream where survey calculations were made.
d. The survey calculation variating pressure and temperature were performed and the calculation report was obtained.

Table 3-2: Input data in OLI Studio for CO_2 partitioning calculations

Input in OLI	
Stream 1	
Pressure, Bar	1
Temperature, ^{0}C	25
Total inflow, Kg	100
MEG concentration relative to water, wt %	0 - 10 - 50

NaOH, mmol	0 - 5
Stream 2	
Pressure, Bar	1
Temperature, ^{o}C	25
CO_2 Inflow, mol	100
CO_2 mole fractions, mol %	0.1 - 1 - 10
Mixer conditions	
Pressure, Bar	1
Temperature, ^{o}C	25
Survey specifications	
Temperature range, ^{o}C	1 - 10
Pressure range, Bar	1 - 100

Figure 3-2 shows the workflow used for the calculations preformed in OLI Studio and Figure 3-3 shows a schematic representation of the calculations performed.

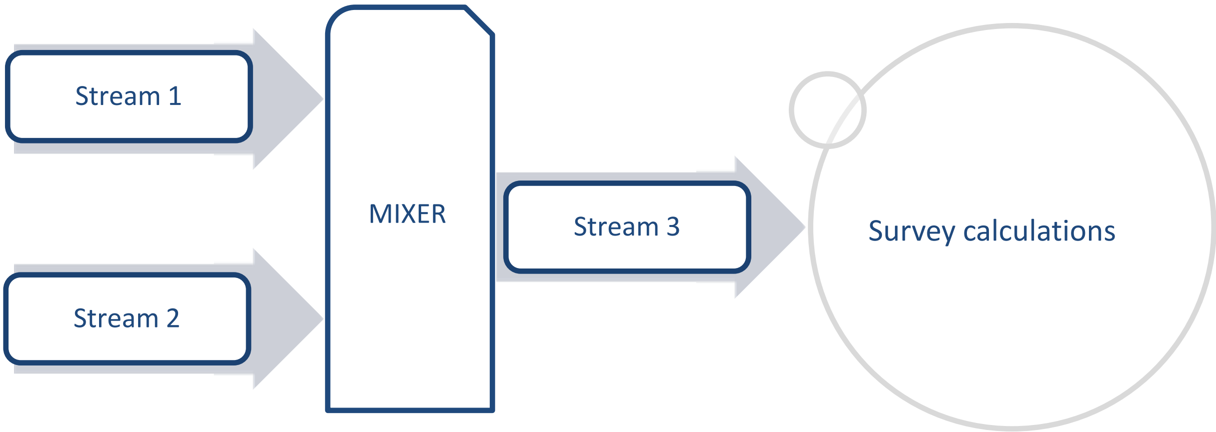

Figure 3-2: Workflow for CO_2 partitioning calculations performed in OLI Studio

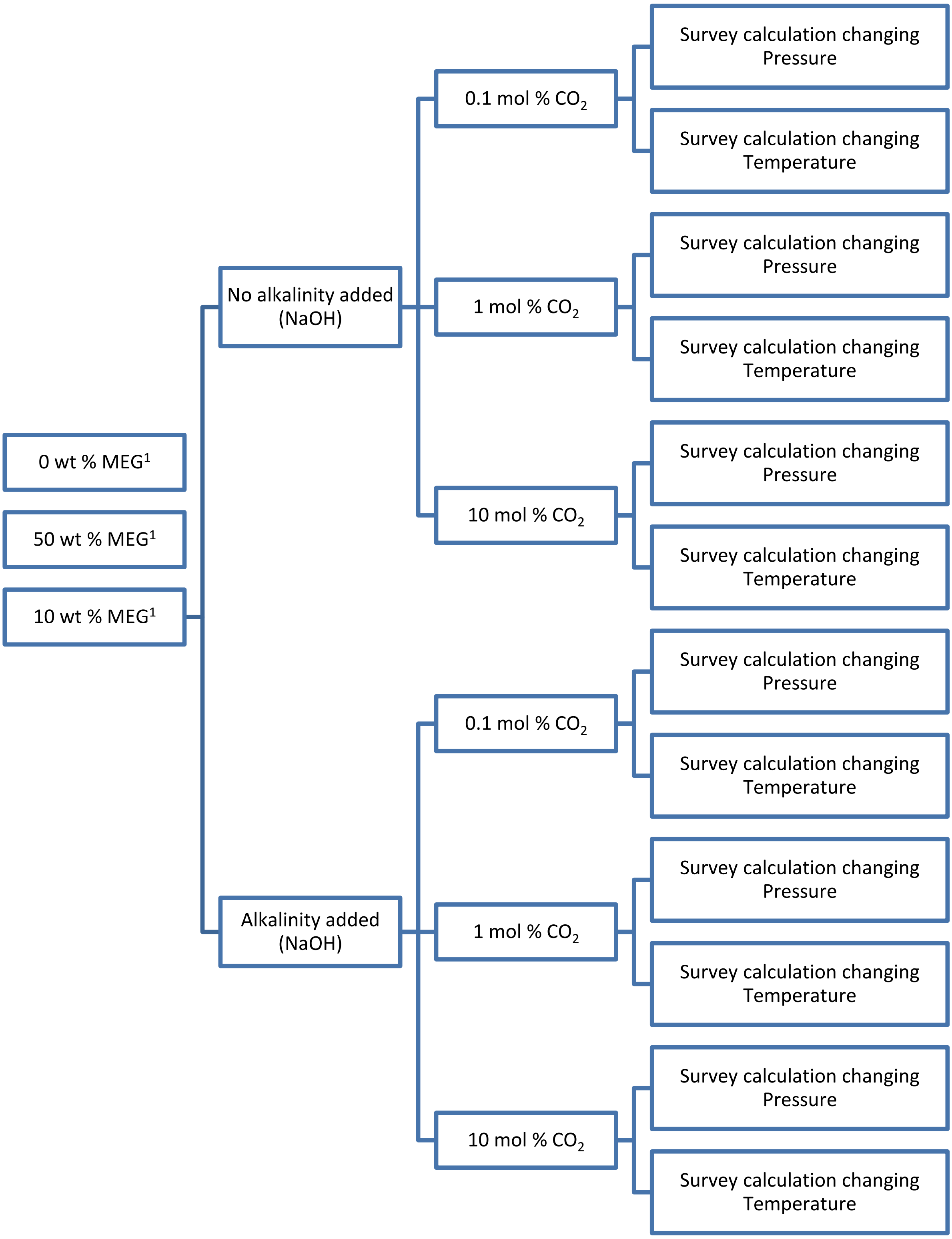

Figure 3-3: Schematic representation of the calculations performed at 10 wt % MEG[1]

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[1] The calculations at 10 wt % MEG are the same calculations performed for 0 wt % MEG and 50 wt % MEG

3.2.2 pH Determination

The pH is an important parameter for ensuring enough precipitation of low solubility salts in the pre-treatment section. This parameter is continuously tracked in a MRU and can be used to determine the injection rate of the alkalinity required to precipitate the low solubility salts. For this reason, pH calculations where done to compare the result given from OLI Studio and from MultiScale.

The data used for the calculation input in OLI Studio and in MultiScale and for evaluating the results was obtained from the experimental work done by K. Sandengen, see Table 3-3 and Table 3-4 [7].

Sandengen's work was reproduced in in OLI Studio and in MultiScale and consisted of pH calculations were done as function of $NaHCO_3$ content in the whole concentration interval up to saturation at 25 ^{0}C and at 80 ^{0}C for solutions of 60 wt % MEG and 90 wt % MEG.

Table 3-3: pH measurements done by K. Sandengen at 25 ^{0}C in solutions of 60 and 90 wt % MEG [7]

$NaHCO_3$, mmol/kg	P_{CO2}, Bar	pH at 60 wt %	Na2HCO$_3$, mmol/kg	P_{CO2}, Bar	pH at 90 wt %
0	0.98	4.13	0	0.99	4.88
19.9	0.98	6.58	1.0	0.99	5.90
99.4	0.98	7.21	9.0	0.99	6.80
199.0	0.98	7.49	47.0	0.99	7.45
298.9	0.98	7.65	104.3	0.99	7.82
399.5	0.98	7.77	164.1	099	7.96
599.0	0.98	7.80	216.9	0.99	8.10
			270.2	0.99	8.20
			313.1	0.99	8.22
			378.5	0.99	8.29
			514.1	0.99	8.30

Table 3-4: pH measurements done by K. Sandengen at 80 ^{0}C in solutions of 60 and 90 wt % MEG [7]

$NaHCO_3$, mmol/kg	P_{CO2}, Bar	pH at 60 wt %	Na2HCO$_3$, mmol/kg	P_{CO2}, Bar	pH at 90wt%
0	0.72	4.76	0	0.88	5.40
3.8	0.72	6.69	0.96	0.88	6.59
12.8	0.72	7.21	8.8	0.88	7.53
60.1	0.72	7.81	46.1	0.88	8.16
114.3	0.72	8.04	92.9	0.88	8.34
273.2	0.72	8.37	180.56	0.88	8.59
394.9	0.72	8.47	297.2	0.88	8.74
584.2	0.72	8.58	452.2	0.88	8.88
751.9	0.72	8.62	666.8	0.88	8.95
1005.5	0.72	8.63	925.1	0.88	8.95
1368.9	0.72	8.64			

Calculations set up MultiScale

The calculations steps were performed in the following manner:

a. Two input streams were made; one for the water-MEG solutions and the other one for CO_2 in gas phase. MultiScale mixes the streams by setting the flow of the two streams higher than 0 m^3/d in the input data.
b. The input data is shown in Table 3-5. The concentration of $NaHCO_3$ in the water-MEG solutions was varied from 0 mmol/kg of solvent to its saturation in the water-MEG solutions. $NaHCO_3$ concentration is not part of the input data in MultiScale. The content of $NaHCO_3$, was varied by changing Na^+, CO_2 and alkalinity concentration.
c. The streams were combined using the single point calculation type in single stream calculation.

Table 3-5: Input data in MultiScale for pH calculations at 25 ^oC and at 80 ^oC in solutions of 60 wt % MEG and 90 wt % MEG

Input in MultiScale				
Stream 1				
Scenario	**a**	**b**	**c**	**D**
Temperature, ^oC	25		80	
Pressure, Bar	1.0135		1.0135	
Rate, m^3/d	100		100	
MEG concentration relative to water, wt %	60	90	60	90
Na^+, total alkalinity and CO_2 concentration, mmol/Kg of Solvent	0	0	0	0
	19.9	1.0	3.8	0.96
	99.4	9.0	12.8	8.8
	199.0	47.0	60.1	46.1
	298.9	104.3	114.3	92.9
	399.5	164.1	273.2	180.56
	599.0	216.9	394.9	297.2
		270.2	584.2	452.2
		313.1	751.9	666.8
		378.5	1005.5	925.1
		514.1	1368.9	
Stream 2				
Scenario	**a**	**b**	**c**	**D**
Pressure, Bar	0.98	0.99	0.72	0.88
Temperature, ^oC	25		25	
Rate, m^3/d	100		100	
CO_2 mole fraction, mol %	100		100	
Mixer conditions				
Scenario	**a**	**b**	**c**	**D**
Pressure, Bar	1.0135		1.0135	
Temperature, ^oC	25		80	

Figure 3-4 shows a schematic overview of the simulations performed.

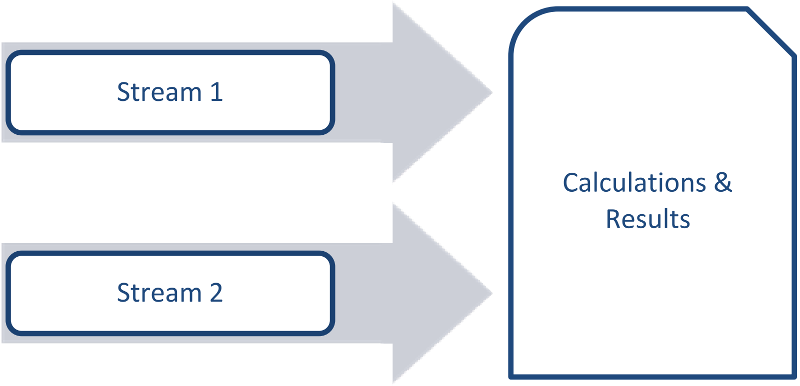

Figure 3-4: Workflow for the pH determination in MultiScale

Calculations set up OLI Studio

The MSE model was used because the solvent consisted of 60 wt % and 90 wt % MEG.

The calculations steps were performed in the following manner:

a. Two input streams were made; one for the water-MEG solutions and the other one for CO_2 in gas phase.
b. The streams were combined using the calculations tool from OLI Studio called Mixer, see Figure 3-5.
c. The input data is shown in Table 3-6. The content of $NaHCO_3$ in the water-MEG solution was varied from 0 kg to its saturation in the water-MEG solution.

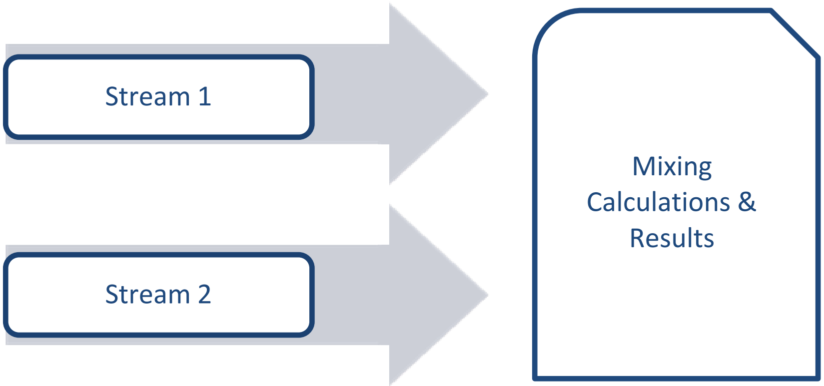

Figure 3-5: Workflow for the pH determination in OLI Studio

Table 3-6: Input data in OLI Studio for pH calculations at 25 ^{o}C and at 80 ^{o}C in solutions of 60 wt % MEG and 90 wt % MEG

Input in OLI Studio				
Stream 1				
Scenario	**a**	**b**	**c**	**D**
Temperature, ^{o}C	25	25	80	80
Water Inflow, Kg	42475.85	10975.04	42475.85	10975.04
MEG Inflow, Kg	63713.78	98775.37	63713.78	98775.37
$NaHCO_3$ Inflow, Kg	0 177.52 886.70 1775.19 2666.36 3563.77 5343.42	0 9.22 82.98 433.33 961.61 1512.95 1999.75 2491.16 2886.69 3489.65 4739.84	0 33.90 114.18 536.13 1019.62 2115.96 3522.73 5211.39 6707.37 8969.63 12211.36	0 8.85 81.13 425.03 856.51 1664.71 2740.09 4169.15 6147.69 8529.14
Stream 2				
Pressure, Bar	0.98	0.99	0.72	0.88
Temperature, ^{o}C	25	25	25	25
CO_2 Inflow, Kg	176.6	176.6	176.6	176.6
CO_2 mole fraction, mol %	100	100	100	100
Mixer conditions				
Pressure, Bar	1.0135	1.0135	1.0135	1.0135
Temperature, ^{o}C	25	25	80	80

As the input format in MultiScale is different as in OLI Studio, the following arrangements were made:

i. The total amount of solvent mass obtained in the calculation report from MultiScale. This amount was used as an input in OLI Studio. As value is given in the calculation report in kilograms, and OLI Studio input unit can be in kilograms, no conversion was needed.

ii. The total mass of $NaHCO_3$ required to obtain the different concentrations of $NaHCO_3$ in solution was calculated.

As the experimental data from K. Sandengen is shown as mmol/kg of solvent, to obtain the mass of $NaHCO_3$, first the concentration of $NaHCO_3$ in mol/kg of solvent was multiply by the mass of solvent, to obtain the moles of $NaHCO_3$ in the solution, the moles of $NaHCO_3$ was multiply by it molecular weight to obtain the mass of $NaHCO_{3.}$, as shown on Equation 10.

iii. The total amount of gas mass was obtained in the calculation report from MultiScale. This value was used as an input in OLI. As this value is given in the calculation report from MultiScale in kilograms, and OLI Studio input unit can be in kilograms, no conversion was needed.

$$m_{NaHCO3}=M_{NaHCO3}x(m_{H2O}+ m_{MEG})x(MW_{NAHCO3}) \div 1000$$

Equation 10: Calculations of $NaHCO_3$ mass for calculating the input data in OLI Studio

Where;
m_{NaHCO3}, is the mass of $NaHCO_{3,}$ Kg
M_{NaHCO3}, is the molality of the $NaHCO_3$, moles/kg of Solvent
m_{H2O}, is the mass of water in the solution, Kg
m_{MEG}, is the mass of MEG in the solution, Kg
$MW_{NAHCO3,}$ is the molecular weight of the $NAHCO_{3,}$ g/mol

For example, K. Sandengen measured the pH of a solution of 60 wt % MEG at 25 ^oC and a concentration of $NaHCO_3$ of 19.9mmol/kg. This concentration was converted to kilograms by multiplying this value by the total mass of solvent obtained from MultiScale calculation report (see Appendix B). The MultiScale calculation report states that total mass of MEG is 63713.78 kg while the total mass of water is 42475.85 kg. The mmols of $NaHCO_3$ was divided by 1000 to obtain this value in mole. Then, it was multiply by the molecular weight of the $NaHCO_3$ (84.006 g/mol) to obtain the grams of $NaHCO_3$ and then divided by 1000, to convert the grams to kilograms. The calculation is shown in Equation 11.

$$19.9 \text{ mmol/kg x } (63713.78 \text{ kg} + 42475.85 \text{ kg}) \text{ x } 84.006 \text{ g/mol} \div 1000000 = 177.52 \text{ kg}$$

Equation 11: Calculation example for input in OLI Studio from MultiScale

3.2.3 Case Study

As mentioned in section 2.4.1, the pre-treatment section of the MRU removes all divalent cations. These cations are removed as carbonates and hydroxide salts. Removal of all divalent cations is essential to prevent scale in the MRU and downstream equipment. This process is done by controlling the temperature and the pH. The purpose of this simulation is to perform typical calculations when designing the pre-treatment section of the MRU with OLI Studio and compare it with MultiScale.

OLI Studio and MultiScale calculations consisted of addition of NaOH 50 wt % to solutions at conditions mentioned in the Table 3-7. This table shows the typical conditions of a solution in the rich MEG storage tank. This solution was mixed with NaOH 50 wt % at different pressures and temperatures to simulate the precipitation of the salts in the pre-treatment section.

Table 3-7: Pressure temperature and solution composition used for Study case calculations

Rich MEG Pressure in the storage tank, bar	1
Rich MEG Temperature in the storage tank, ^{0}C	40
wt % MEG	0, 20 and 50
Na^{+}, mmol/kg	437
K^{+}, mmol/kg	13.7
Mg^{+2}, mmol/kg	0.21
Ca^{+2}, mmol/kg	0.97
Cl^{-}, mmol/kg	444
CO_2, mmol/kg	13.80
HCO^{-3}, mmol/kg	8.80

The calculations in MultiScale were performed by *Fjords Processing* and the same calculations were then performed with OLI Studio, using the same input.

Calculations set up OLI Studio

The AQ model was used for the calculations performed at 0 wt % MEG and the MSE model was used for the calculations with solutions containing MEG.

As the input format in OLI studio and in MultiScale varies, the following calculation steps were done:

a. Two streams were created one for the NaOH 50 wt % solution and another for the water-MEG solutions.
b. A mixer was added to mix the two streams at wanted pressure and temperature. The mixer method used was a multiplier; which varied the mass of NaOH 50 wt % stream from 0 kg to 240 kg.

The following arrangements were made to create the water-MEG stream:

i. The water analysis tool was used for adding the water-MEG composition; this tool was used because the composition was given as concentration of ions in the solution.
The unit mmol/kg is not available in OLI Studio; therefore the calculation on Equation 12 was made to obtain the total amount of moles in the solution. The mass of water and the mass of MEG was obtained from the MultiScale calculation report.

$$N_i = M_i x(m_{H2O} + m_{MEG})$$

Equation 12 Calculation of moles of ions in the solution

Where;

N_i, is the moles of ‘i’, moles

M_i, is the molality of ‘i’, moles/kg of Solvent

m_{H2O}, is the mass of water in the solution, kg

m_{MEG}, is the mass of MEG in the solution, kg

ii. The no reconciliation type of calculation was made to ensure that the solution was balanced and then add the result was copy to a stream using a tool from OLI Studio called: add as a stream. This was done to perform survey calculations.

Figure 3-6 shows the workflow used for the calculations preformed in OLI Studio, and the input data in OLI Studio is shown in Table 3-8, Figure 3-7 and Figure 3-8.

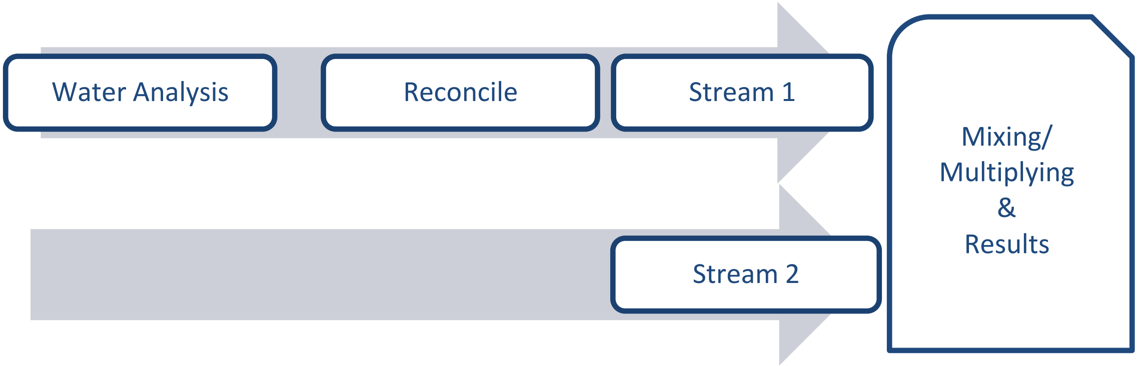

Figure 3-6: Workflow for the study case calculations in OLI Studio

Table 3-8: Input data in OLI Studio for Study case calculations

Input in OLI	
Water Analysis input	
Pressure, Bar	1
Temperature, °C	40
Total inflow, Kg	989.17
MEG concentration relative to water, wt %	0 - 10 – 50
CO_2, mol	13.65
Na^+, mol	432.27
K^+, mol	13.55
Mg^{+2}, mol	0.21
Ca^{+2}, mol	0.96
Cl^-, mol	439.45
HCO^{-3}, mol	8.7
Stream 1	
Pressure, Bar	1
Temperature, °C	40
Total inflow, Kg	100 000
Stream 2	
Pressure, Bar	1

Temperature, °C	25
NaOH 50 wt % inflow, kg	2 – 240
Mixer conditions[2]	
Pressure, Bar	1 – 2
Temperature, °C	30 – 100

The input data in Figure 3-7 and Figure 3-8 is based on the calculations performed in MultiScale provided by *Fjords Processing*.

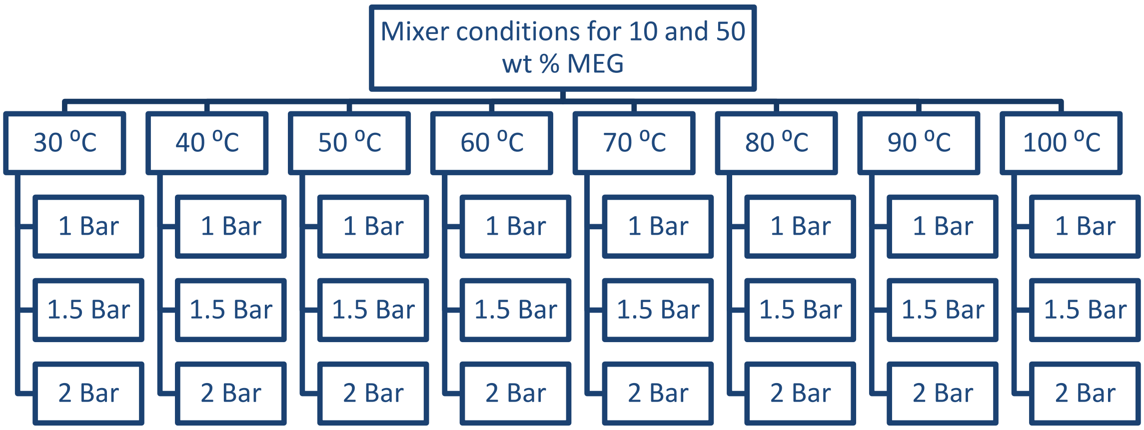

Figure 3-7: Schematic representation of each mixing calculation condition for 10 and 50 wt % MEG performed in OLI Studio

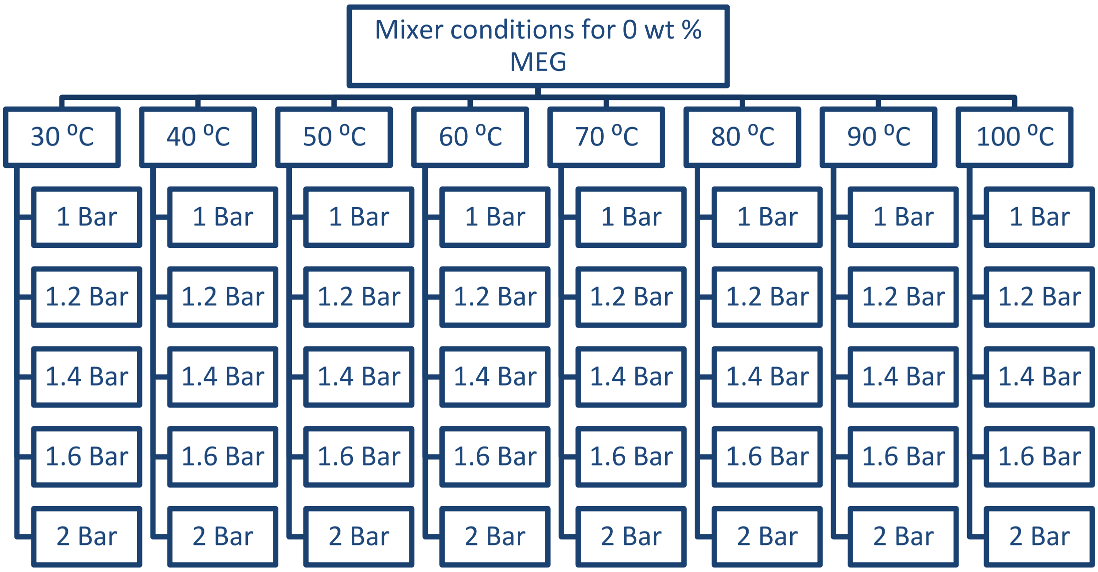

Figure 3-8: Schematic representation of each mixing calculation condition for 0 wt % MEG performed in OLI Studio

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[2] See Figure 3-7 and Figure 3-8 for detailed information of the mixing conditions

4 Results and Discussion

This chapter provides results from all evaluations conducted. Each set of evaluation is followed by interpretations and implications of the results in a design of a MRU.

4.1 CO_2 Partitioning

In this section, the results from the CO_2 partitioning calculations in OLI Studio (section 3.2.1) are compared with the results in MultiScale. The CO_2 partitioning depends on the conditions of the rich MEG storage tank; therefore, the parameters evaluated were pH, pressure, temperature and CO_2 concentration in the gas phase.

4.1.1 pH and Temperature

As stated in the theory section, pH is an important parameter related to the speciation of CO_2. Low pH solutions are dominant by CO_2 and HCO_3^- while high pH solutions are dominant by HCO_3^- and CO_3^{-2}. As Rich MEG pH depends on its component and conditions, it is of interest to know if OLI Studio and MultiScale differ at solutions with different pH values.

Figure 4-1 shows the speciation of CO_2, in water at low pH (4.5-5 pH) calculated with OLI Studio and MultiScale and Figure 4-2 shows the speciation of CO_2 in water with NaOH for observation of the results at higher pH (7-8 pH) calculated with OLI Studio and MultiScale. Both figures are plotted on a logarithmic scale.

Figure 4-1 shows that the data in MultiScale for the concentration of CO_3^{-2} in the solution is slightly lower than the data in OLI Studio at values close to 100 ^oC. This could be due to the difference between the two models at temperature close to ebullition, when CO_2 gradually escape to the gas phase. This difference is considered of no value because this solution is at low pH and in low pH solutions, CO_3^{-2} is not the dominant specie, consequently these concentrations are at very low. With respect to CO_2 and HCO_3^-, Figure 4-1 shows that OLI Studio and MultiScale correspond at the whole temperature interval calculated.

With regard to higher pH calculations (7-8 pH), Figure 4-2 shows that the concentration of the CO_2, HCO_3^- and CO_3^{-2} in OLI Studio and MultiScale correspond at the whole temperature interval calculated. As CO_2, HCO_3^- and CO_3^{-2} are dominant at approximately neutral pH it is valuable to see that OLI Studio and MultiScale are matching at the whole temperature range.

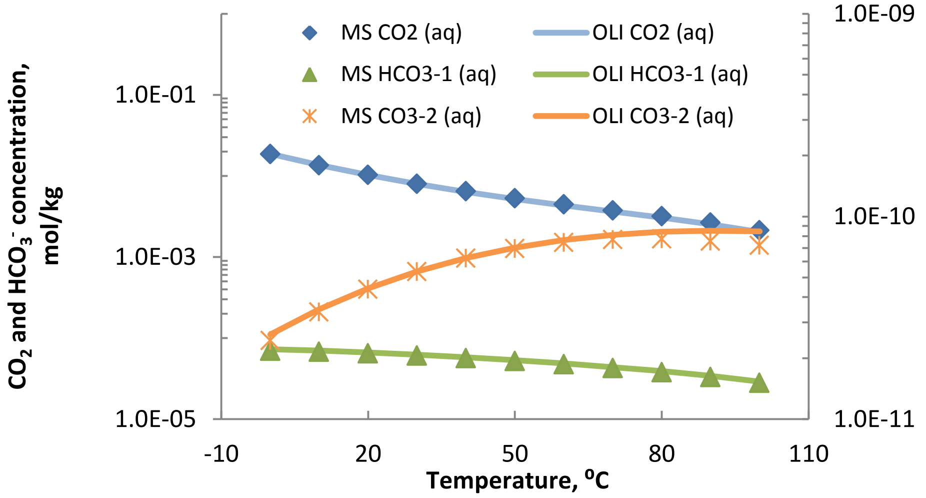

Figure 4-1: Dissolved CO_2, HCO_3^- and CO_3^{-2} in pure water as a function of temperature at 3 bar and a pH range from 4.5 to 5. CO_2 content in the gas phase is 10 mol %

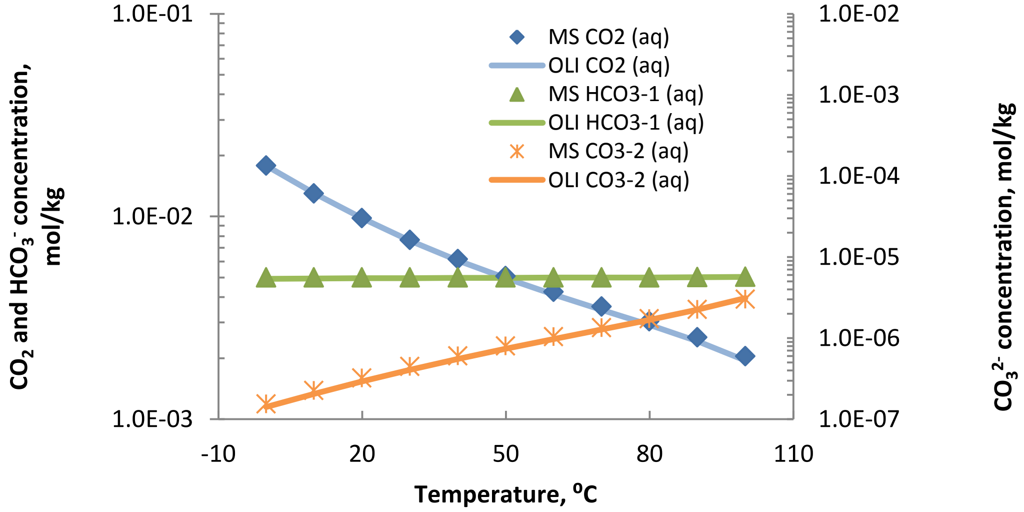

Figure 4-2: Dissolved CO_2, HCO_3^- and CO_3^{-2} in a solution of water with NaOH as a function of temperature at 3 bar and a pH range from 7 to 8. CO_2 content in the gas phase is 10 mol %

It was also relevant to observe if the speciation of CO_2 in 10 wt % MEG and 50 wt % MEG in OLI Studio and in MultiScale was different at different pH, therefore, the calculation results of the speciation of CO_2 in 10 wt % MEG and 50 wt % MEG at different pH values were also plotted and are shown from Figure 4-3 to Figure 4-6.

From Figure 4-3 to Figure 4-6, it is observed that there is a slightly offset for the concentration of CO_2 and CO_3^{-2} for all the solutions evaluated in these figures at the whole interval of the temperature calculated. Unlike the concentration of HCO_3^- in OLI Studio and in MultiScale, this matches at the whole temperature range.

As Figure 4-3 to Figure 4-6, show the same behaviour, it seems that the difference in the concentration of CO_2 and CO_3^{-2} is due to the concentration of MEG.

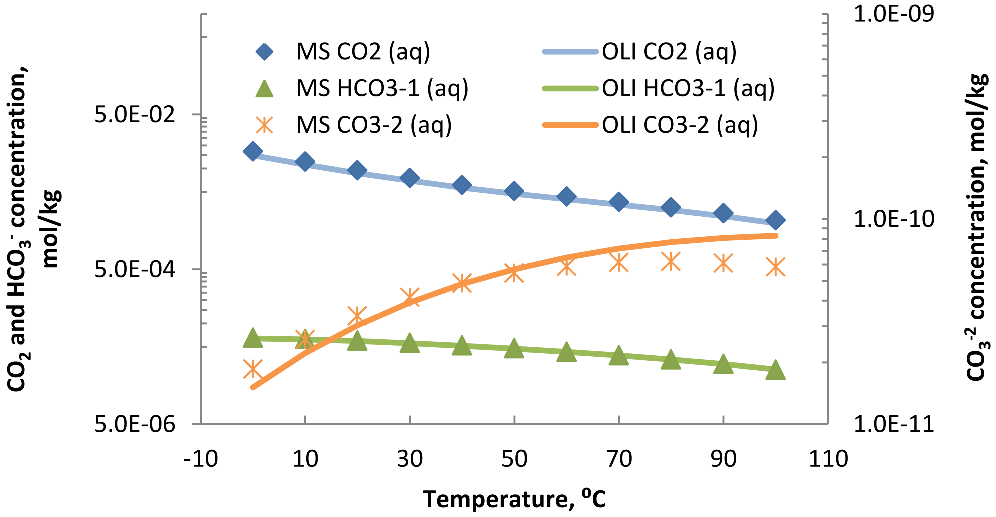

Figure 4-3: Dissolved CO_2, HCO_3^- and CO_3^{-2} in a solution of 10 wt % MEG with NaOH as a function of temperature at 3 bar and a pH range from 4.1 to 4.6. CO_2 content in the gas phase is 10 mol %

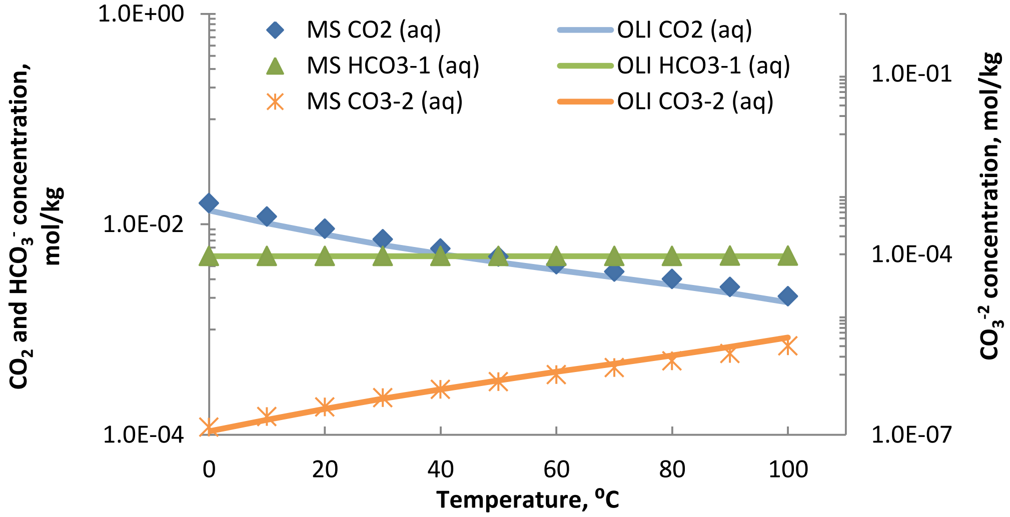

Figure 4-4: Dissolved CO_2, HCO_3^- and CO_3^{-2} in a solution of 10 wt % MEG with NaOH as a function of temperature at 3 bar and a pH range from 6.0 to 6.9. CO_2 content in the gas phase is 10 mol %

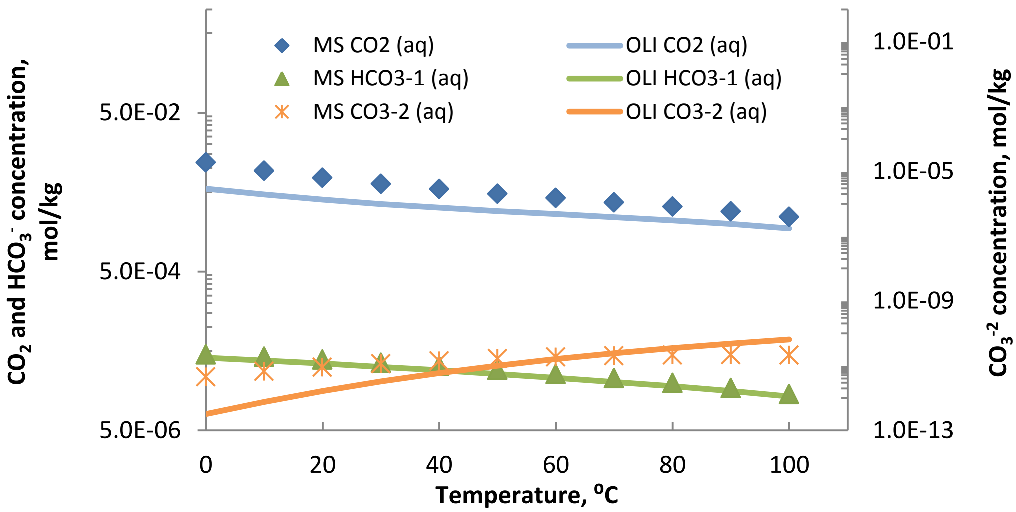

Figure 4-5: Dissolved CO_2, HCO_3^- and CO_3^{-2} in a solution of 50 wt % MEG as a function of temperature at 3 bar and a pH range from 4.1 to 4.6. CO_2 content in the gas phase is 10 mol %

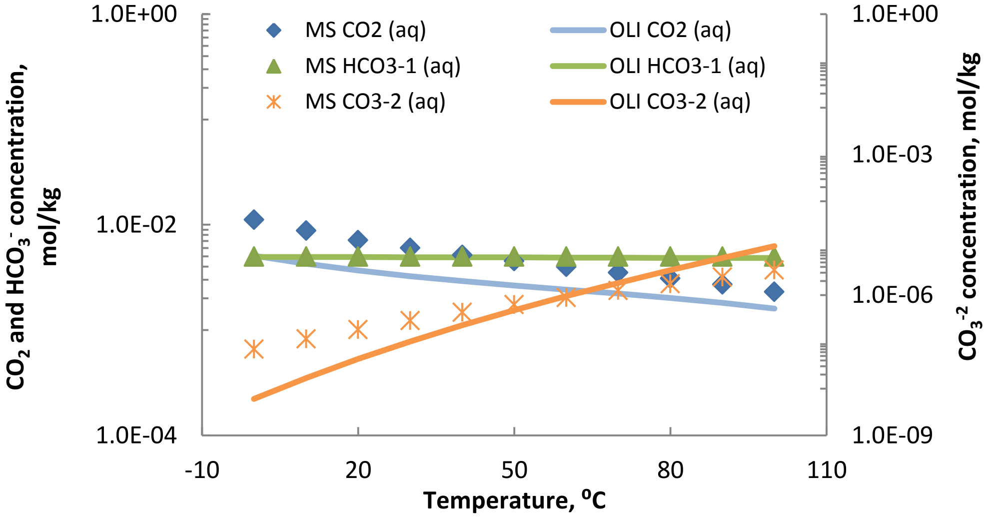

Figure 4-6: Dissolved CO_2, HCO_3^- and CO_3^{-2} in a solution of 50 wt % MEG as a function of temperature at 3 bar and a pH range from 6.1 to 7.0. CO_2 content in the gas phase is 10 mol %

These figures appear that for water and water-MEG solutions at 3 bar and 10 mol % of CO_2 in the gas phase, the discrepancies between OLI Studio and MultiScale are depended the MEG concentration. Speciation of CO_2 was also plotted at other pressures and CO_2 concentration in the gas phase and the results were the same. These figures are shown in Figure C-1 to Figure C-8 in Appendix C.

4.1.2 CO_2 Partial Pressure

As the amount of dissolved gas is proportional with the its partial pressure in the gas phase and CO_2 partial pressure is proportional to its concentration. CO_2 concentration in the liquid phase as function of different concentrations of CO_2 was evaluated.

Figure 4-7 to Figure 4-9 show the CO_2 concentration in the liquid phase as function of the temperature for water and water-MEG solutions at different concentrations of CO_2 in the gas phase. The plot is made on a logarithmic scale.

These figures show that the difference between OLI Studio and MultiScale increases with the MEG concentration. It is also noted that the higher the temperature the lower the discrepancies between OLI Studio and MultiScale, as the pre-treatment section of the MRU operates at high temperatures, this could result in similar results when designing the MRU.

It is also observed from these figures that as stated on the theory section, the concentration of CO_2 decreases with the temperature. In addition, while decreasing the concentration of CO_2 the concentration of CO_3^{-2} is increasing, complying with Le Châtelier's Principle.

Moreover, it is also of worth to point out that the dissolved CO_2 in water-MEG solutions in OLI Studio is lower than MultiScale. As mentioned in the theory section, the equilibrium constant of a reaction in equilibrium is calculated by dividing the molal concentration of the products by the molal concentration of the reactants. The equilibrium constant for the dissociation of H_2CO_3 to HCO_3^- is higher that the equilibrium constant for dissociation of HCO_3^- to CO_3^{2}. It means that the more CO_2 is dissolved in the solution, the more HCO_3^- is present in the solution and the more OH^- is required to convert the HCO_3^- to CO_3^{2-}. As more CO_2 dissolved is predicted by MultiScale, this seems to indicate that more addition of NaOH is to be predicted by MultiScale than to OLI Studio to convert the CO_2 to CO_3^{2-} . This was evaluated in the case study.

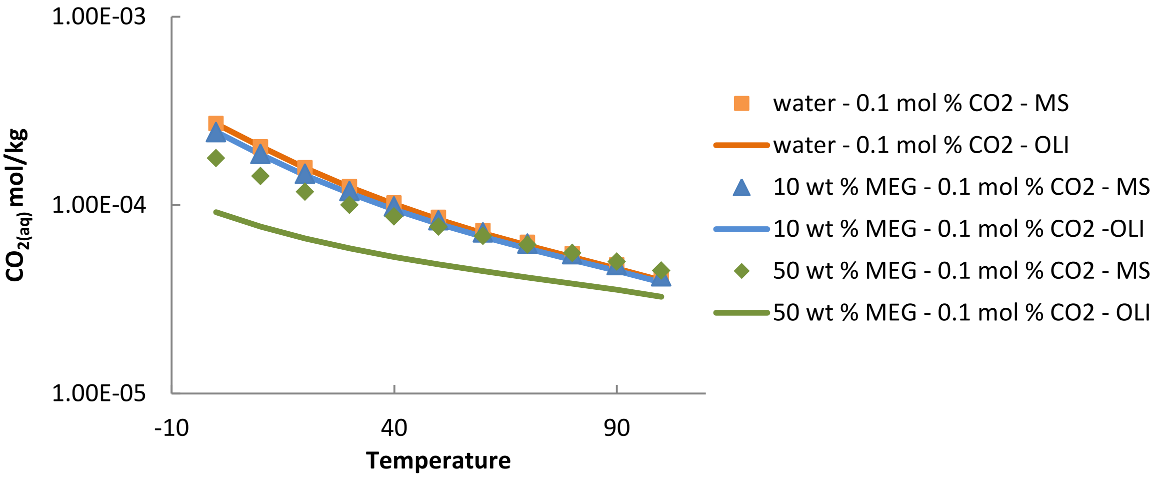

Figure 4-7: Dissolved CO_2 as a function of temperature for solutions of different MEG content 0.1 mol % CO_2 concentrations in the gas phase at 5 bar

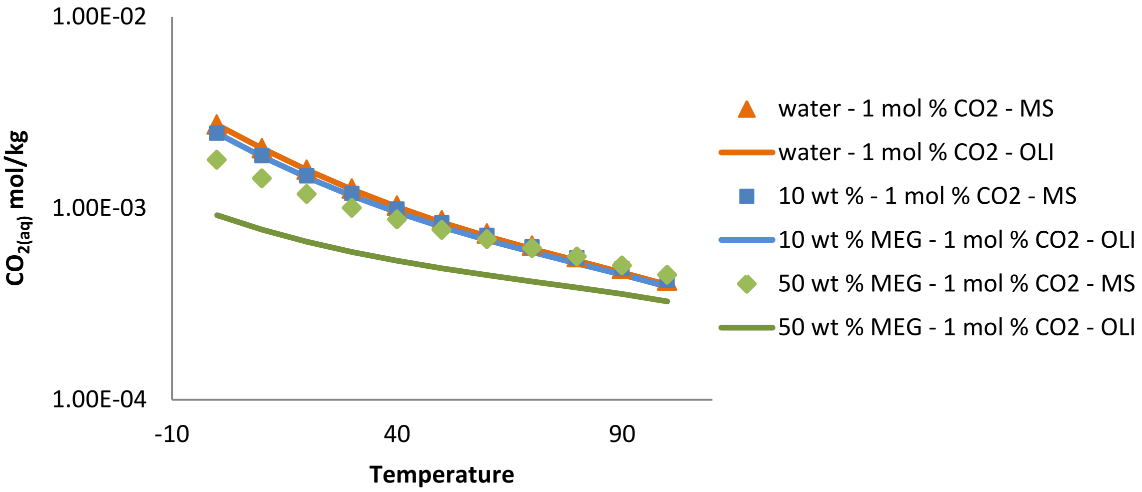

Figure 4-8: Dissolved CO_2 as a function of temperature for solutions of different MEG content 1 mol % CO_2 concentrations in the gas phase at 5 bar

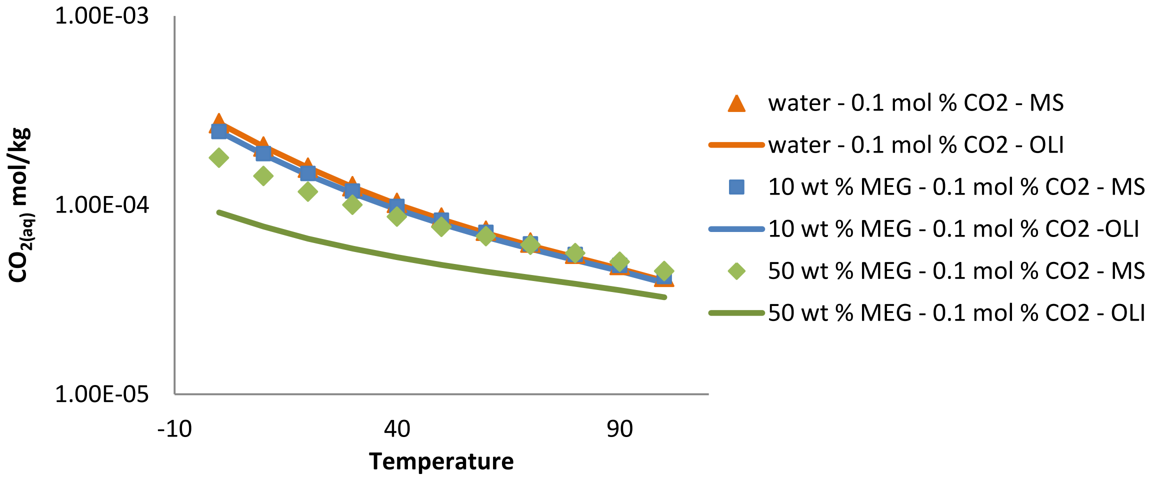

Figure 4-9: Dissolved CO_2 as a function of temperature for solutions of different MEG content 10 mol % CO_2 concentrations in the gas phase at 5 bar

4.1.3 Pressure

Figure 4-10 to Figure 4-12 were also made for the CO_2 speciation in water and water-MEG solutions as function of the pressure at 80 ^{0}C and 10% CO_2 in the gas phase. Calculations were done at 80 ^{0}C to observe the CO_2 partitioning difference at the operating temperature of the pre-treatment section of the MRU. It is plotted on a logarithmic scale. This parameter is also important because speciation of the CO_2 also depends on the pressure.

Figure 4-10 to Figure 4-12 illustrate that as expected, the CO_2 concentration in the liquid phase increases with the pressure. It also shows that OLI Studio and MultiScale correspond at the whole range of pressure calculated for water solutions.

For water-MEG solutions (Figure 4-11 and Figure 4-12), it is observed that there is a slightly offset for the concentration of CO_2 and CO_3^{-2} at the whole interval of the temperature calculated, this offset is bigger for solutions at 50 wt % MEG than for 10 wt % MEG. This offset is not observed for the water solutions (Figure 4-10). Also the concentration of HCO_3^- in OLI Studio and in MultiScale complies for the solutions evaluated at the whole pressure range. As identified previously, the difference in these graphs can be due to the concentration of MEG. In the case study it is observed whether or not these discrepancies are significant.

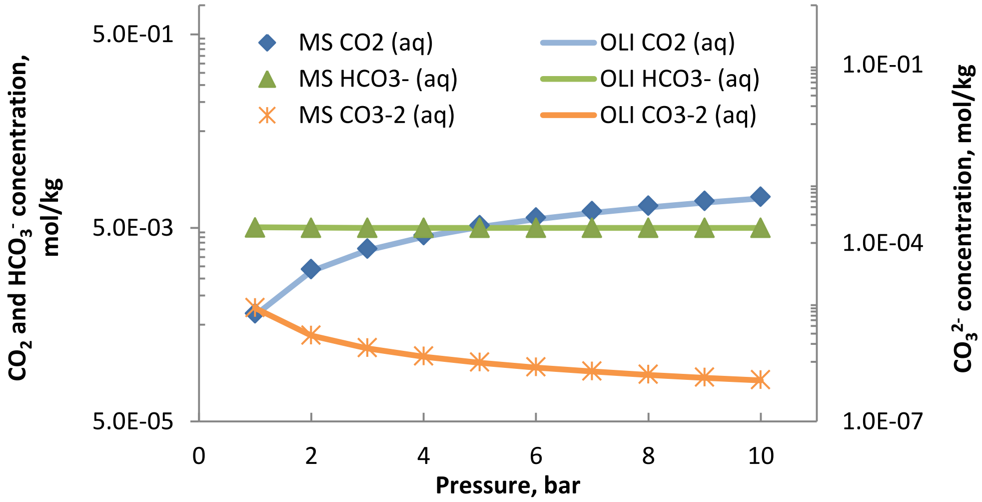

Figure 4-10: Dissolved CO_2, HCO_3^- and CO_3^{2-} as a function of pressure in solution of water at 80 ^{0}C and pH range from 6 to 8. 10 mol % CO_2 concentration in the gas phase

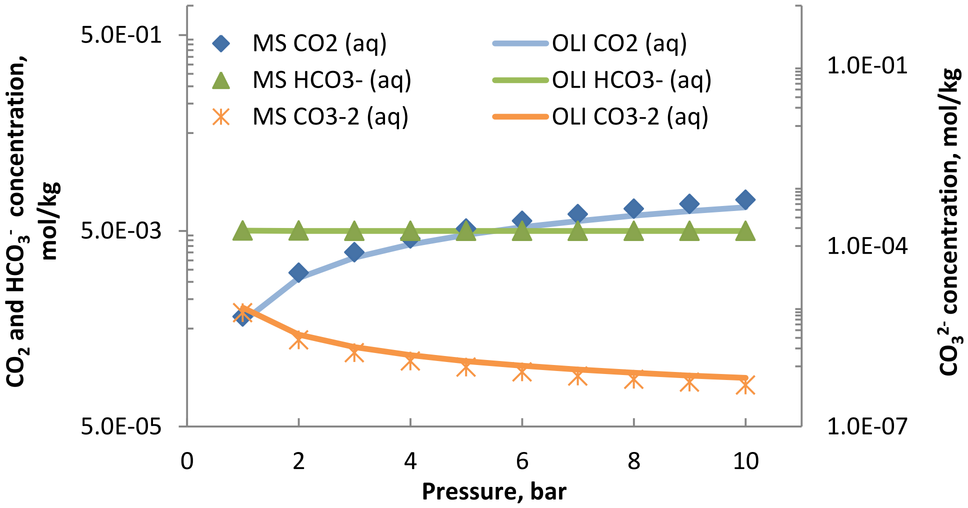

Figure 4-11: Dissolved CO_2, HCO_3^- and CO_3^{2-} as a function of pressure in solution of 10 wt % MEG at 80 °C and pH range from 6 to 8. 10 mol % CO_2 concentration in the gas phase

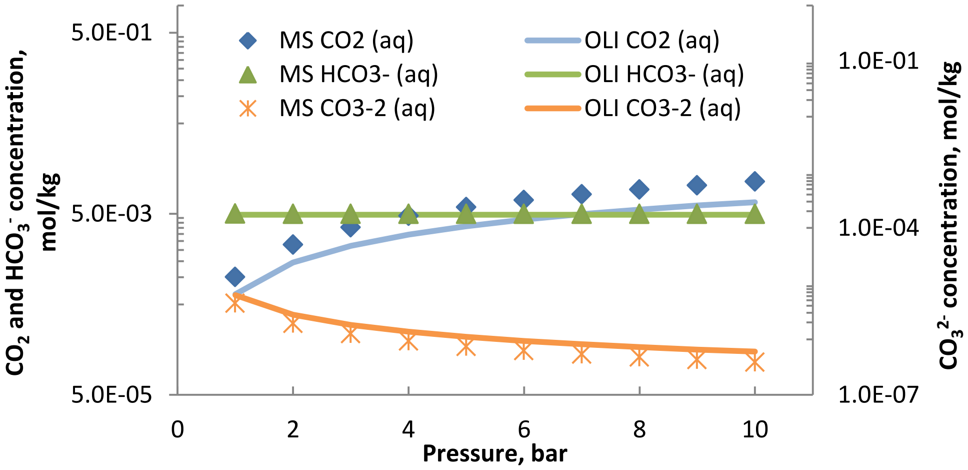

Figure 4-12: Dissolved CO_2, HCO_3^- and CO_3^{2-} as a function of pressure in solution of 50 wt % MEG at 80 °C and pH range from 6 to 8. 10 mol % CO_2 concentration in the gas phase

4.2 pH Determination

In this section, the results from Section 3.2.2 were compared with the pH measurements done by K. Sandengen [7].

Comparing experimental pH values with the predicted pH values is important because discrepancies between predicted pH and measured pH can lead to economic, environmental and safety issues. For example, if the predicted pH is lower than the measured pH, the estimated alkalinity, required for prediction of precipitation of low solubility salts in the pre-treatment vessel, will be higher than the minimum required, what will lead to higher consumption of chemicals and therefore higher cost. On the other hand, if the predicted pH is higher than the measure pH, the estimated alkalinity required for prediction of precipitation of low solubility salts in the pre-treatment vessel will be lower than the minimum required and it may lead to formation of scaling in most sections of the MEG regeneration unit. It can contribute to blockage of valves, filters, pumps, pipes, among others issues that consequently impact the environment and the safety of all organism around.

One factor considered to evaluate the difference between OLI Studio and MultiScale is the instrument error. A pH electrode error may be as little as 0.05 pH units up to 0.5 pH units [51].

As mentioned in Section 2.4.3, the pH provided in the OLI Studio results report is defined as water-based and an alternative method for calculating pH of systems in which water is not a dominant solvent was used (Equation 9). The Equation 9 and OLI Studio calculation reports were used for calculating the solution pH in OLI Studio.

The pH data obtained from OLI Studio simulation report (OLI), OLI Studio Equation 9 (OLI equation), MultiScale (MS), and experimental values from K. Sandengen [7] for 60 wt % and 90 wt % MEG solutions were plotted as function of the $NaHCO_3$ concentration at 25 ^oC and at 80 ^oC and it are shown from Figure 4-13**Error! Reference source not found.** to Figure 4-16.

Figure 4-13 to Figure 4-16 show that reported pH in OLI Studio deviate from pH calculations in MultiScale and the experimental pH measurements by K. Sandengen by approximately 0.7 pH units. However, it is shown that the OLI Studio calculated pH with Equation 9 is corresponding with the experimental pH measured by K. Sandengen and the calculated pH obtained from MultiScale calculation report.

Figure 4-13 and Figure 4-14 show that at 25 ^oC this difference between OLI Studio (Equation 9), MultiScale and experimental values from K. Sandengen is considered minor as their differences are less than 0.3 pH units. This is based on typical pH measurements errors [51].

Difference between the experimental pH from K. Sandengen and the MultiScale model is not expected because the work performed by K. Sandengen is used for constructing the model in MultiScale[7]. Nevertheless, Figure 4-15 and Figure 4-16 show that at 80 ^oC a bigger difference is observed (0.7-0.9 pH units). This difference is observed at low pH values, when the $NaHCO_3$ concentration is 0 mmol/Kg . This difference could have an impact in the design of the MRU if the Rich MEG from the storage tank has a low pH. For example, Figure 4-15 shows that experimental pH by K. Sandengen at 0 mmol/Kg is higher than the predicted pH. It means that the model would predict lower amount of CO_2 dissolved and therefore higher alkalinity dosing will be predicted than required. Table D-2 to Table D-5 in Appendix D show the pH reported by MultiScale and the experimental pH by K. Sandengen.

Figure 4-15 and Figure 4-16 shows that at $NaHCO_3$ concentration higher than 40 mmol/kg, the predicted data from OLI Equation 9 is approximately 0.2 pH units lower than the data in MultiScale and the experimental data obtained from K. Sandengen [7]. The reason of why the pH is lower in OLI could be due to the lower predicted concentration of CO_2 dissolved by OLI model. This is shown on the CO_2 partitioning calculations section.

As pH obtained in MultiScale and the pH obtained with Equation 9 using the results from OLI Studio were in general within 0.1pH units difference, it can be stated that pH obtained from both simulations reproduces the experimental pH obtained from K. Sandengen.

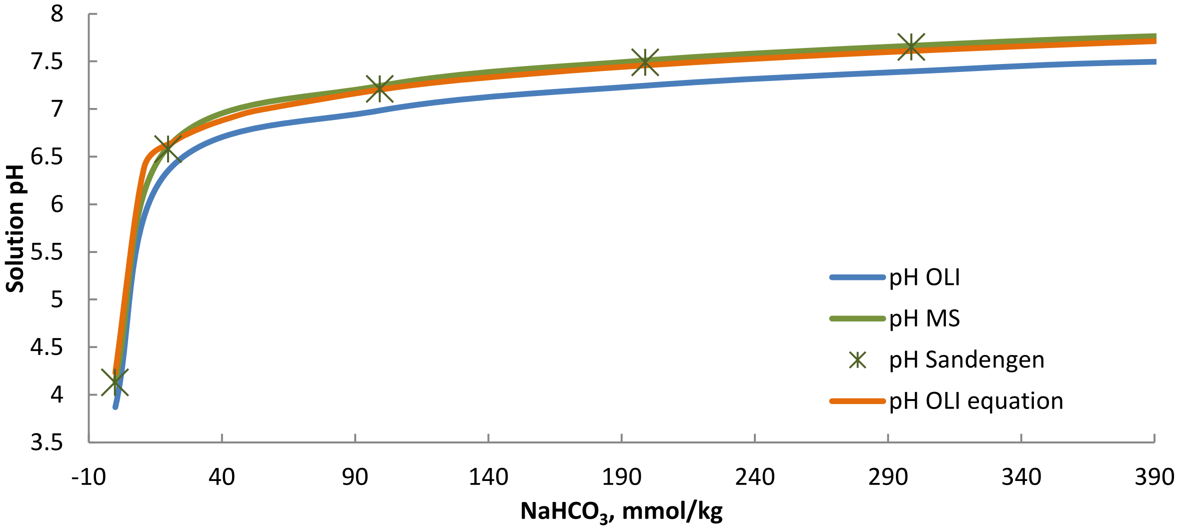

Figure 4-13: pH as function of $NaHCO_3$ obtained from OLI simulation report (OLI), OLI (OLI equation 12), MultiScale (MS), and experimental values from K. Sandengen [7] at 25 ^{o}C in solutions of 60 wt % MEG and 0.98 bar P_{CO2}

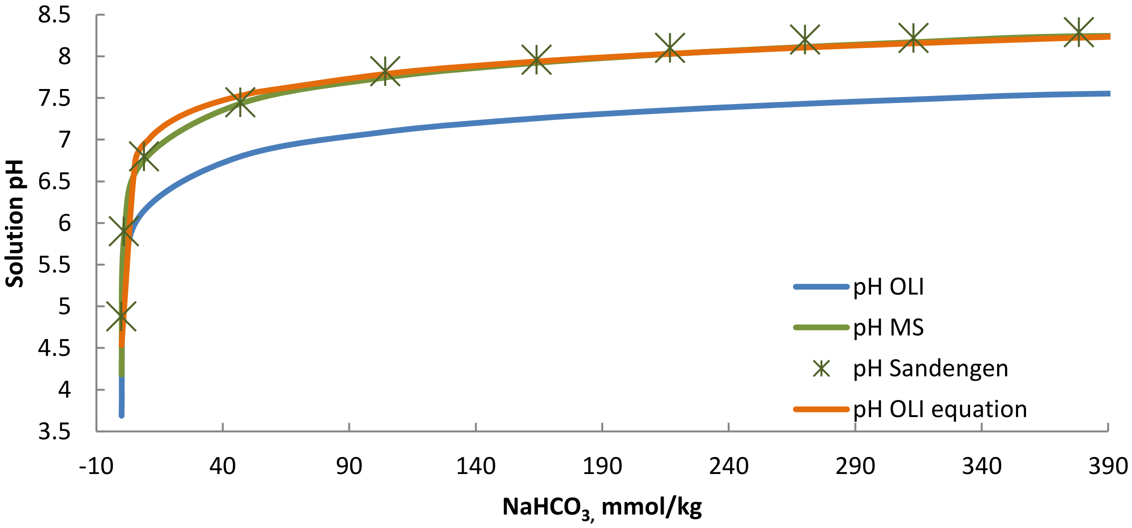

Figure 4-14: pH as function of $NaHCO_3$ obtained from OLI simulation report (OLI), OLI (OLI equation), MultiScale (MS), and experimental values from K. Sandengen [7] at 25 ^{o}C in solutions of 90 wt % MEG and 0.99 bar P_{CO2}

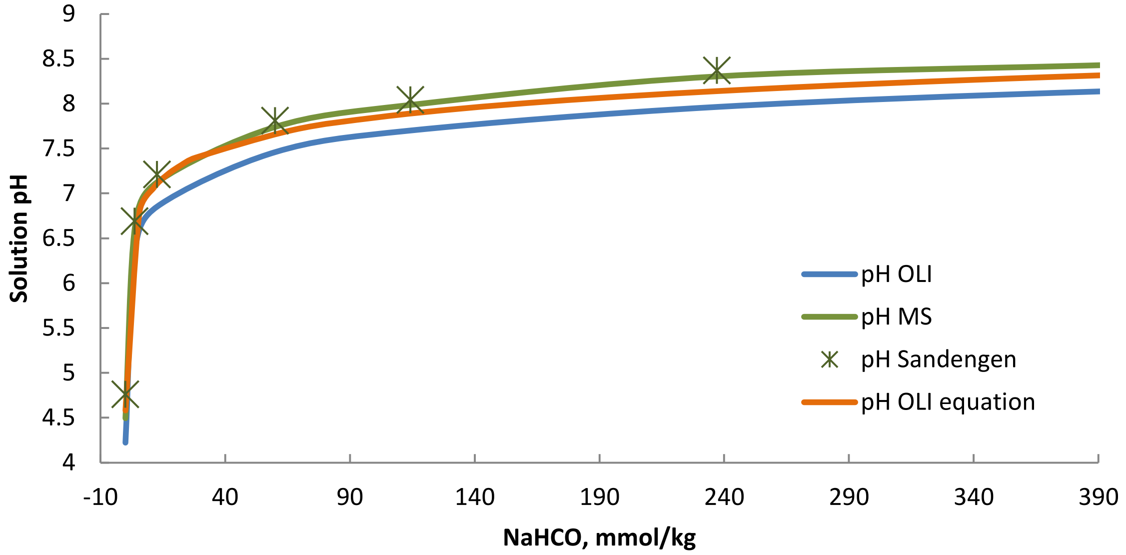

Figure 4-15: pH as function of $NaHCO_3$ obtained from OLI simulation report (OLI), OLI (OLI equation 12), MultiScale (MS), and experimental values from K. Sandengen [7] at 80 ^{0}C in solutions of 60 wt % MEG and 0.72 bar P_{CO2}

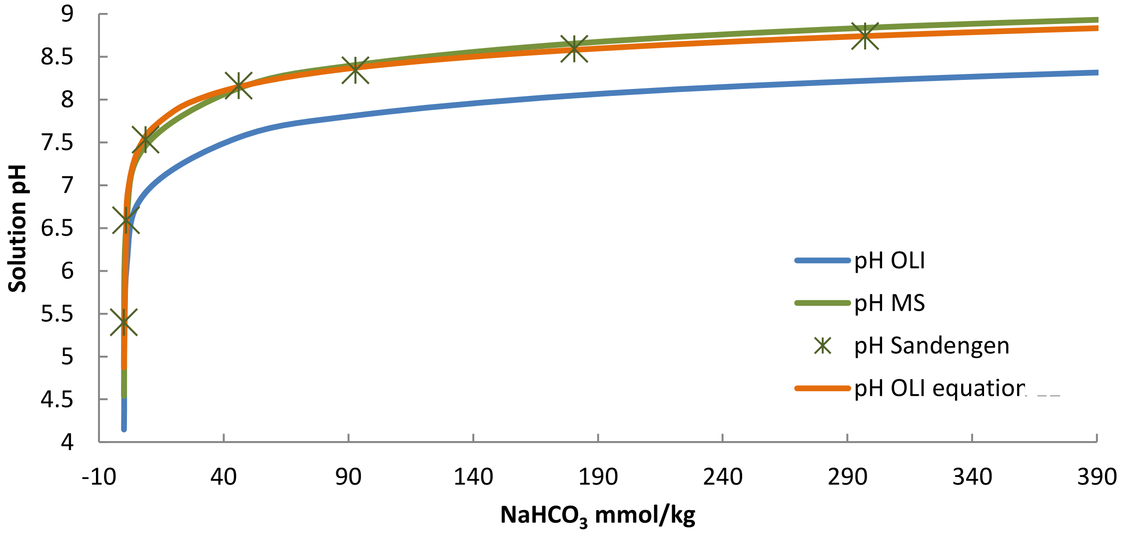

Figure 4-16: pH as function of $NaHCO_3$ obtained from OLI simulation report (OLI), OLI Equation 9 (OLI equation 9), MultiScale (MS), and experimental values from [7] at pH at 80 ^{0}C in solutions of 90 wt % MEG and 0.88 bar P_{CO2}

4.3 Case Study

In this section the results from the case study calculations in OLI Studio (section 0) are compared with the results in MultiScale. This section consisted of typical design calculations of the pre-treatment section of the MRU. The main purpose of the pre-treatment is to remove the low solubility salts, in this case they are Ca^{+2} and Mg^{+2}. These salts are removed by increasing the pH to 9.6 and the temperature to 80 ^{o}C according to the reference [4]. Therefore, this section is divided in the parts pH analysis, calcium ions removal analysis and magnesium ions removal analysis.

It is worth mentioning that one of the arguments considered for foreseeing whether or not the difference is significant, is the typical design margin. As design uncertainties arise from uncertainties in the design data available, a design factor is often included to ensure that the design meets products specification and allow flexibilities. According to the NORSOK standard P-100, equipment design margin are typically 10 % or more [52, 53].

Also, as mentioned in previous sections, the typical pH electrode errors were taken into account to determine the significance of the discrepancy; these errors can be up to 0.5 pH units [51].

4.3.1 pH Analysis

In previous sections it was noted that the pH computed in OLI Studio (Equation 9) and in MultiScale do not different significantly. The intention of this section is to verify that previous calculation results are in concordance with the study case calculation results.

Figure 4-17 shows the largest pH difference between OLI Studio and MultiScale in the whole NaOH concentration evaluated in solutions of water, 20 wt % MEG and 50 wt % MEG at 30 ^{o}C, 50 ^{o}C and 80 ^{o}C for water and water MEG solutions at 1 bar. These three temperatures were chosen to observe the difference in the results at different temperatures.

As observed in CO_2 partitioning section, Figure 4-17 shows that the largest pH difference between OLI Studio and MultiScale increased by MEG content and decrease with temperature. Also it is observed that the pH difference in this section is higher than the difference observed in section 4.2. This discrepancy could be due to difference between their salt content and the difference between their scale prediction models. Appendix D, Figure D-10 to Figure D-18 show the pH as function of NaOH concentration in water and water-MEG solution at 30 ^{o}C, 50 ^{o}C and 80 ^{o}C and 1 bar.

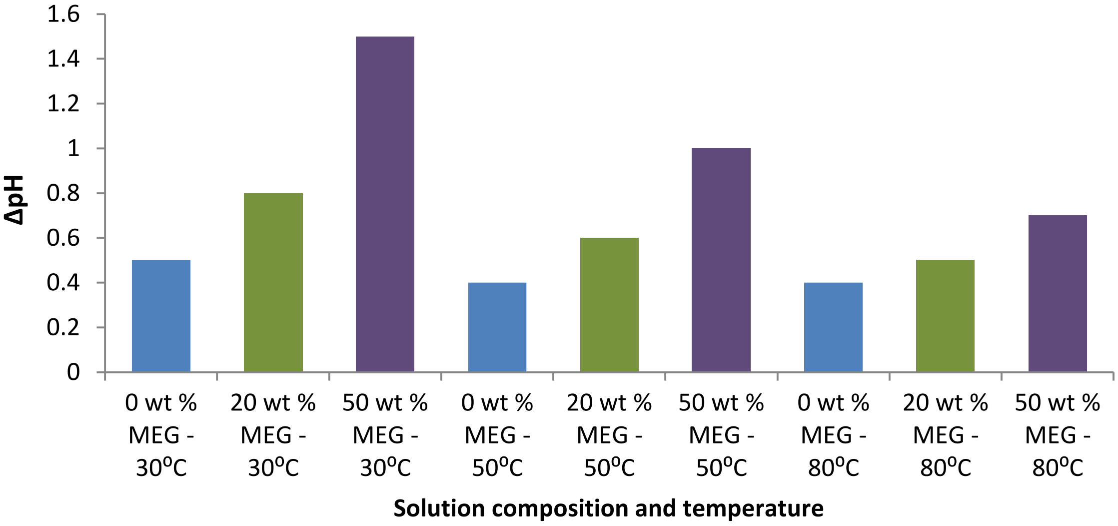

Figure 4-17: Largest pH difference between OLI Studio and MultiScale at water and water-MEG solutions at 30 ºC, 50 ºC and 80 ºC and 1 bar.

To evaluate the largest differences, solution pH was plotted as function of NaOH concentration at 50 wt % MEG solution at 30 ºC and 1 bar. See Figure 4-18.

Figure 4-18 shows that the pH from OLI Studio differs from MultiScale for more than 1 pH unit, it means that more NaOH is required for one of these simulation software to reach the same pH. For example, to reach a 9.5 pH in the pre-treatment section, OLI Studio predicts a NaOH concentration of 15.2 mmol/kg of solution while MultiScale predicts a concentration of 18.9 mmol/kg of solution. The difference between OLI Studio and MultiScale at this pH is 3.7 mmol/kg of solution. If we take into consideration that Rich MEG inlet rate of 100 tons/d, it means that 60.8 kg of NaOH is predicted by OLI Studio while 75.6 kg of NaOH is predicted by MultiScale. As MultiScale predicts 24 % more alkalinity and it exceeds typical design margin calculations, this difference seems to be significant.

Given this results, it might be necessary to mentioned that for solutions at this conditions, other approaches technique could be used to ensure a good design of the MRU. For example, compare these results with experimental results (lab experiments or pilot experiments). This is necessary to minimize the use of chemicals and ensure correct removal of the desired salts. Nevertheless, operating temperature of the pre-treatment section is typically higher than 30ºC; therefore this discrepancy might not be relevant when designing MRUs.

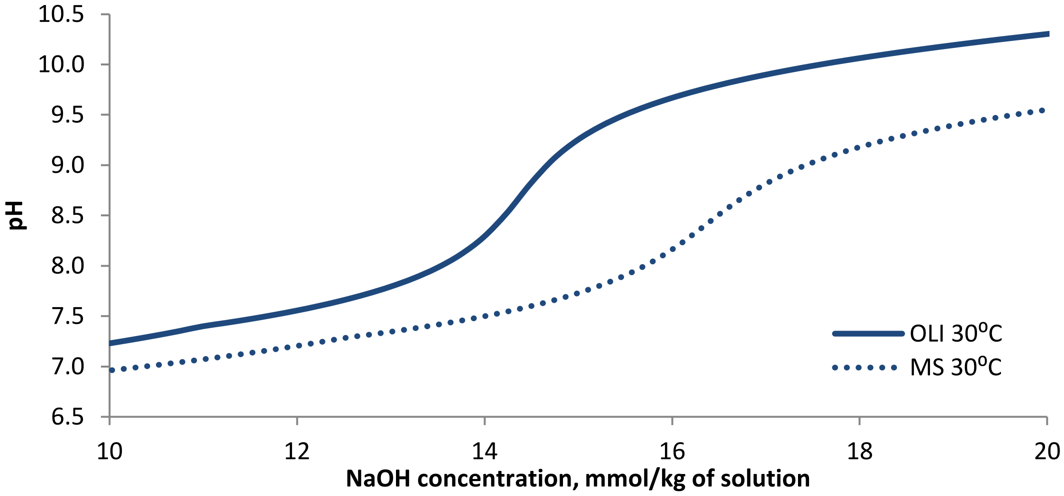

Figure 4-18: pH as function of NaOH concentration in 50 wt % MEG solution at 30 °C and 1 bar

As normal pre-treatment temperature is 80 °C, solution pH was plotted as function of NaOH concentration at 50 wt % MEG solution at 80 °C and 1 bar. See Figure 4-19.

At normal operating conditions, Figure 4-19 shows that the pH difference between OLI Studio and MultiScale is less than 0.7 pH unit. As an example, to reach a 9.5 pH in the pre-treatment section, OLI Studio predicts a NaOH concentration of 28.68 mmol/kg of solution while MultiScale predicts a concentration of 28.58 mmol/kg of solution. At this pH, the difference between OLI Studio and MultiScale at this pH is 0.1 mmol/kg of solution. For a Rich MEG inlet rate of 100 tons/d, it means that 69.5 kg of NaOH is predicted by OLI Studio while 69.7 kg of NaOH is predicted by MultiScale. As the additional amount required by MultiScale represents an additional 0.34 % of NaOH. As the difference between these software is very low. Also as the difference is significantly lower than 10 %, it is observed that under normal operating conditions, OLI Studio and MultiScale pre-treatment design calculation is in concordance.

It is also noted that the pH predicted by OLI Studio is higher that the pH predicted by MultiScale, what also in concordance with the Section 4.1.1 as the CO_2 concentration predicted in OLI Studio was lower that the CO_2 concentration predicted by MultiScale.

Moreover, in this section is also noted that the higher the temperature the lower the difference between OLI Studio and MultiScale.

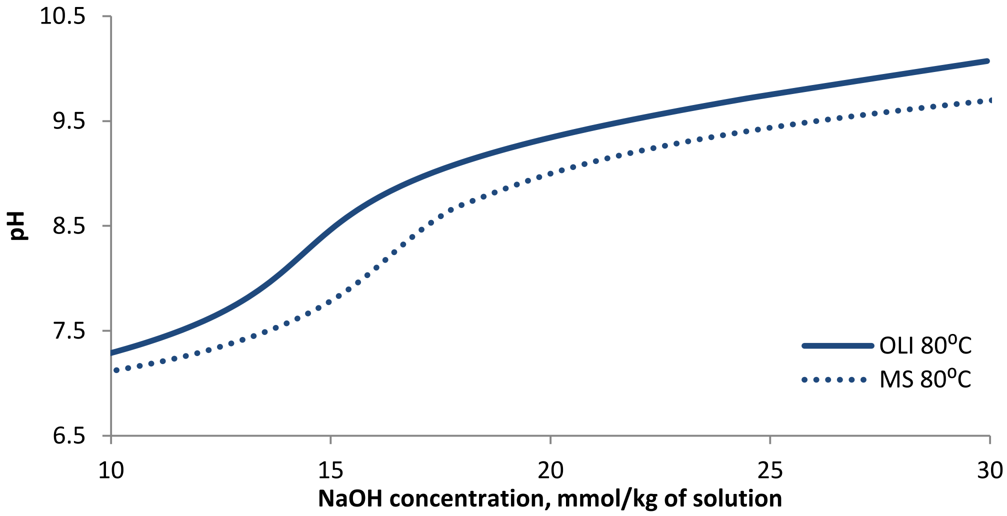

Figure 4-19: pH as function of NaOH concentration in 50 wt % MEG solution at 80 ^{o}C and 1 bar

4.3.2 Calcium Ions (Ca^{2+})

Calcium ions removal effectiveness relay on the prediction of the alkalinity dosing required for precipitating it as calcium carbonate, the alkalinity added can be controlled by measuring the solution pH of the pre-treatment vessel. In addition, the amount of $CaCO_3$ precipitated is calculated to design the dimensions/capacity of the Rich MEG centrifuge and also it can give an estimate of how often should the equipment have maintenance. Maintenance of a rich MEG centrifuge is usually based on manufacture's recommendations and it can be based on the amount of solid treated.

Figure 4-20 shows the Ca^{2+} concentration and $CaCO_3$ precipitation rate as function of the solution pH in 50 wt % MEG solution at 80 ^{o}C and 1 bar.

It is important to remark that as shown on Figure 4-20, the initial Ca^{2+} concentration is lower in OLI Studio than in MultiScale. This mismatch appears to be occurring because of the setting of the calculations in OLI Studio and MultiScale. As presented in section 0, the input format in OLI Studio and in MultiScale is very different. It leaded to difference in the initial Ca^{2+} concentration of about 2.5 %.

In Figure 4-20, OLI Studio indicates that a slightly higher pH is required to precipitate the calcium carbonate. Nevertheless, the difference between the calculated pH in both software is less than 0.5 pH units at the whole concentration of Ca^{2+} evaluated. Considering that pH electrodes can gives an error as high as 0.5 pH units [51], the difference between OLI Studio and MultiScale is considered insignificant. This finding is very important because it means that both software will predict the same solution pH to decrease the concentration of Ca2+ in the pre-treatment section.

With regard to the precipitated $CaCO_{3,}$ Figure 4-20 shows that the highest difference between the models is less than 1 kg of $CaCO_3$ precipitated, since the total amount of $CaCO_3$ precipitated is no more than 10.3 kg. The difference between OLI Studio and MultiScale correspond to less than 10 %. The maximum amount of $CaCO_3$ precipitated is 10 % higher in MultiScale than in OLI Studio. In addition, the initial concentration of Ca^{2+} is 2.5 % higher in MultiScale than in OLI Studio, it seems that the net difference between OLI Studio and MultiScale is approximately 7.5 %. As typical standard design margin are 10 %, this difference seems to be not significant. Nevertheless, as design margin is a design factor used to cover uncertainties, evaluation of the significance of this difference may depend on the type of the centrifuge used and also the design margin recommended by the centrifuge manufacture.

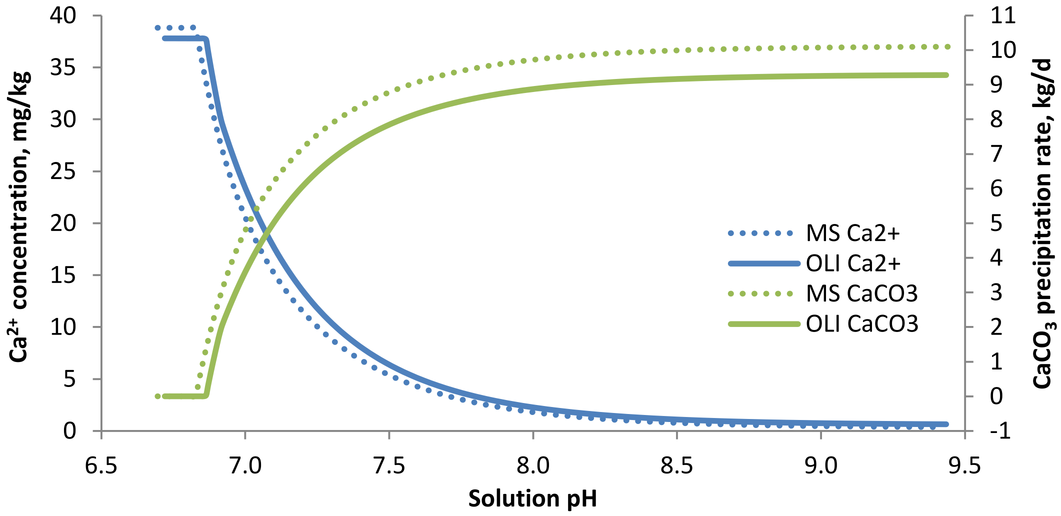

Figure 4-20: Ca2+ concentration and $CaCO_3$ precipitation rate as function solution pH in water at 50 °C and 1 bar according to OLI Studio and in MultiScale

Beside pH difference, alkalinity dosing was also evaluated, Figure 4-21 shows the NaOH concentration required to obtain a Ca^{2+} concentration of 5 mg/kg of solution and $CaCO_3$ in water and water-MEG solutions at 30, 50 and 80 °C and 1 bar. This table shows that as predicted from CO_2 partitioning calculations (section 4.1), the difference between OLI Studio and MultiScale increases with MEG concentration and decreases with the increase temperature. Moreover, it is observed that MultiScale predicts a higher addition of alkalinity to precipitate the calcium carbonate. This is in concordance with the CO_2 partitioning calculation as the concentration of CO_2 in the aqueous phase was higher in MultiScale than in OLI Studio.

At a Ca^{2+} concentration of 5 mg/kg of solution, the difference of NaOH injection in MultiScale and in OLI Studio is from 1.0 mmol/kg to 2.1 mmol/kg (see Figure 4-21). Provided that the flow rate is 100 tons/d, a difference of 2.1 mmol/kg corresponds to an 8.4 kg/d. This difference occurs for solutions at 50 wt % MEG at 30 °C. At this condition the NaOH concentration in the solution in OLI Studio and in MultiScale is 14.0 mmol/kg and 16.1 mmol/kg respectively. It means a difference of 13.9 %, this difference seems to be considerable. Moreover, at MRU normal conditions (50 wt % MEG and 80 °C), the NaOH concentration in the solution in OLI Studio and in MultiScale is 12.2 mmol/kg and 13.5 mmol/kg respectively, this represents a difference of 10 %, taking into consideration that it seems to be an input difference of 2.5 %, these difference seems to be not significant as a 10 % design margin will cover uncertainties in the mass required to precipitate the salts in the pre-treatment. Nevertheless, this discrepancy may be significant in other aspects of the design but it would have to be evaluated case by case.

Appendix E, Figure E-19 to Figure E-27 show $CaCO_3$ SR in water and in water-MEG solutions as function of the pH at different temperatures.

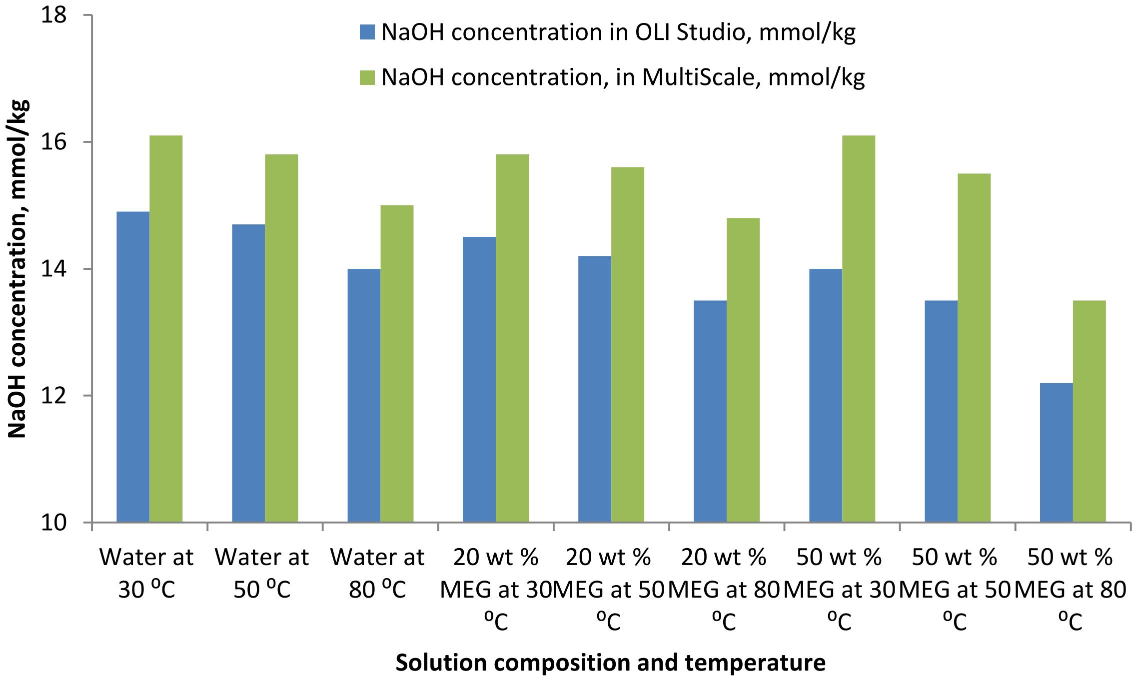

Figure 4-21: NaOH concentration required to decrease the Ca^{2+} concentration from approximately 38 mg/kg to 5 mg/Kg in water and water-MEG solutions at 30 °C 50 °C and 80 °C and 1 bar according to OLI Studio and MultiScale

Figure 4-22 to Figure 4-24 show the $CaCO_3$ SR in water and in water-MEG solutions as function of the pH at different temperatures. The graphs are plotted at a logarithmic scale to appreciate the discrepancies between OLI Studio and MultiScale at saturation ration equal to 1 unit (when the calcium carbonate is saturated).

The largest pH difference observed in the graphs is not higher than 0.5 pH unit. No significant difference is observed in the prediction of $CaCO_3$ SR as function of the pH in the conditions evaluated.

It is also noted that the $CaCO_3$ SR in MultiScale is higher than in OLI Studio for solutions at pH higher than 7 pH units (after saturation of calcium carbonate). This result is expected because due to difference in input format in the software, the initial concentration of Ca^{2+} is higher in MultiScale than in OLI Studio. This is also in concordance with the results from Figure 4-20 as more precipitated $CaCO_3$ was estimated by MultiScale than in OLI Studio.

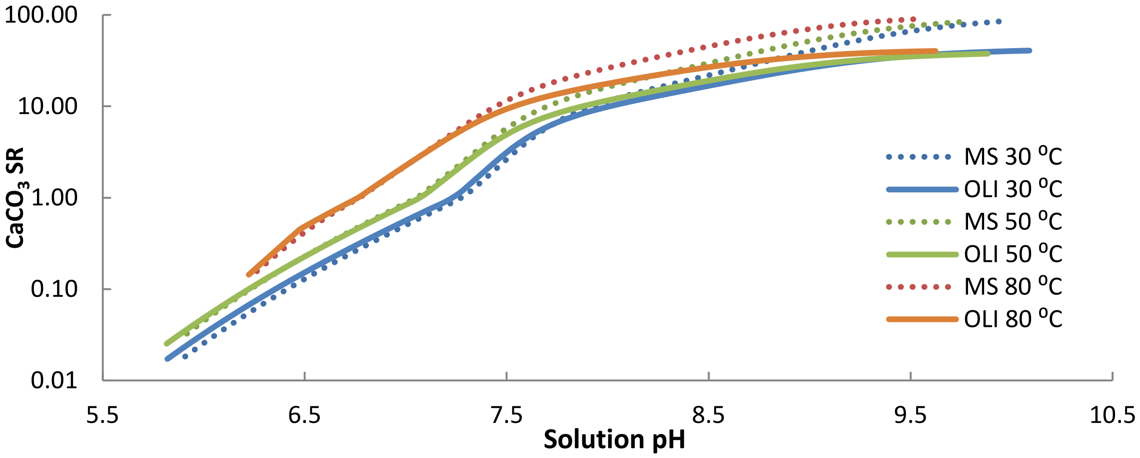

Figure 4-22: $CaCO_3$ SR as function of the solution pH in water at 30 °C, 50 °C and 80 °C and 1 bar

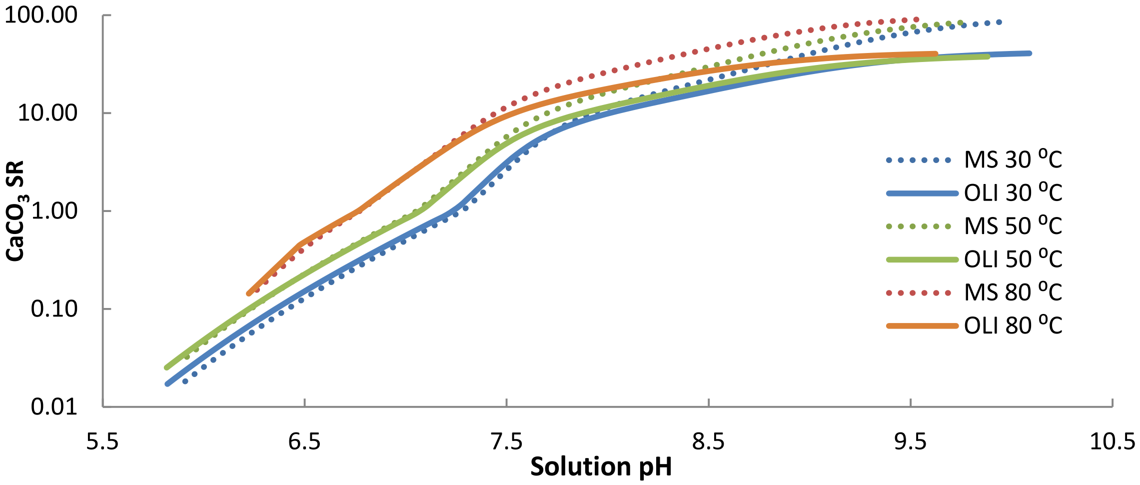

Figure 4-23: $CaCO_3$ SR as function of NaOH concentration in 20 wt % MEG solution at 30 °C, 50 °C and 80 °C and 1 bar

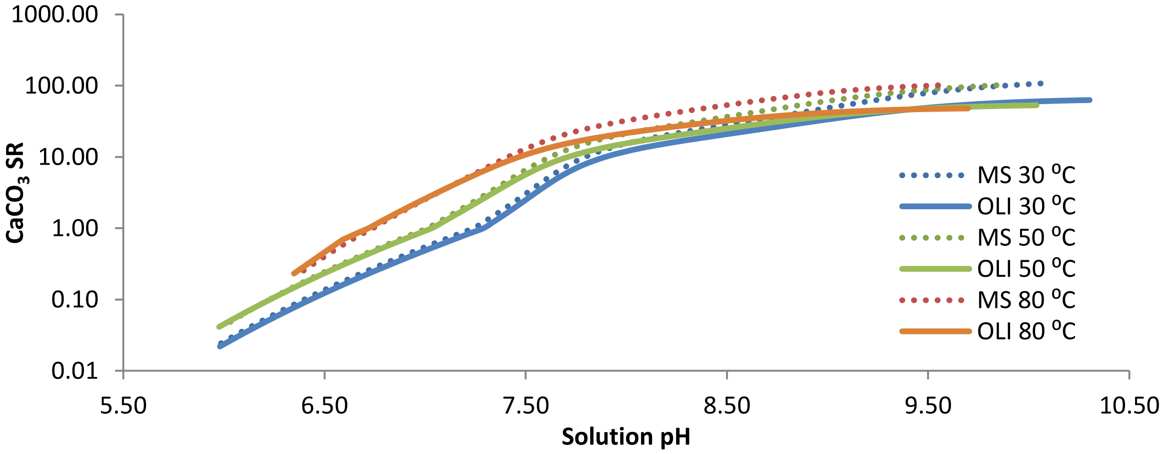

Figure 4-24: $CaCO_3$ saturation ratio as function of NaOH concentration in 50 wt % MEG solution at 30 °C, 50 °C and 80 °C and 1 bar

4.3.3 Magnesium Ions (Mg^{2+})

Magnesium ions removal effectiveness also relays on the prediction of the alkalinity dosing. The removal is done by precipitating it as magnesium hydroxide in the pre-treatment vessel. In Addition, the amount of $Mg(OH)_2$ precipitated is calculated to design the dimensions/capacity of the Rich MEG centrifuge and also it can give an estimate of how often should the equipment have maintenance. Maintenance of a rich MEG centrifuge is usually based on manufacture's recommendations and it can be based on the amount of solid treated. Figure 4-25 shows the Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of the solution pH in 50 wt % MEG solution at 80 ^{o}C and 1 bar.

As arose for the Ca^{2+} concentration, Figure 4-25 shows that the initial Mg^{2+} concentration is lower in OLI Studio than in MultiScale. This mismatch occurred because of different input format in OLI Studio and in MultiScale. The difference in the initial Mg^{2+} concentration is approximately 0.9 mg/kg of solution. As the initial Mg^{2+} concentration is 5 mg/kg of solutions, the initial concentration difference between these software is about 20 %. Taking into consideration the initial concentration of magnesium ions is very low and OLI and MultiScale input format is different, significant difference between these too software is expected.

Figure 4-25 indicates a notable difference between OLI Studio and MultiScale in the prediction of the required pH in the solution to precipitate $Mg(OH)_2$. For instance, according to MultiScale the $Mg(OH)_2$ start precipitating at a pH of 8.6, while OLI Studio predicts a pH of 9.7. As typical pH electrode errors are no higher than 0.5 pH units, this difference is significant. Consequently, the $Mg(OH)_2$ precipitation rate also differs considerably.

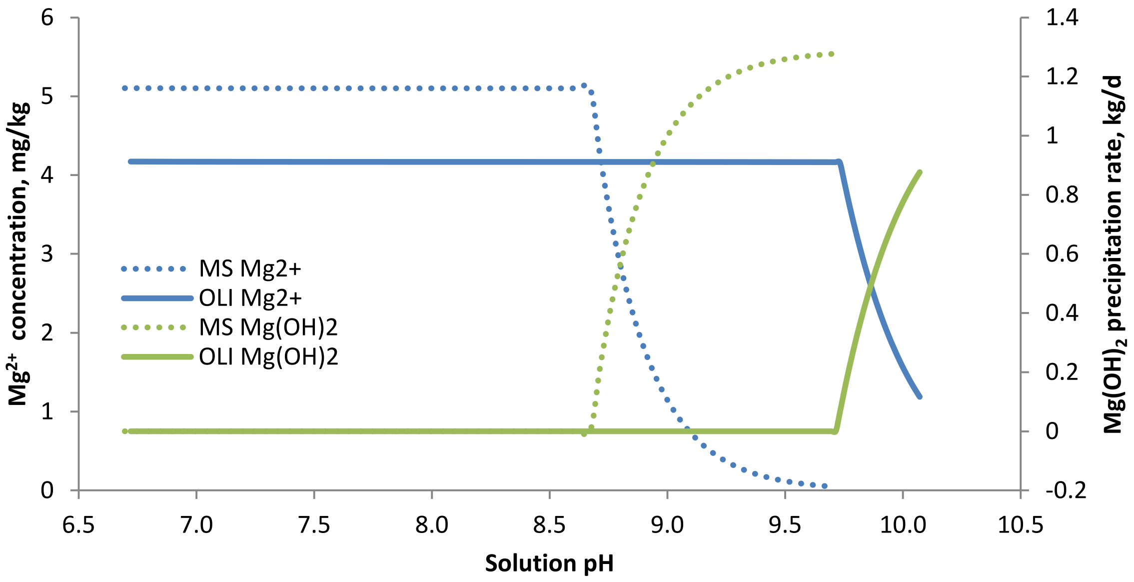

Figure 4-25: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function solution pH in 50 wt % MEG at 80 ^{o}C and 1 bar

Figure 4-26 to Figure 4-28 show the $Mg(OH)_2$ SR in water and in water-MEG solutions as function of the solution pH at 30 ^{o}C, 50 ^{o}C and 80 ^{o}C. The graphs are made at a logarithmic scale to appreciate the discrepancies between OLI Studio and MultiScale at saturation ration equal to 1 unit (when the $Mg(OH)_2$ is saturated).

These figure shows that the $Mg(OH)_2$ SR in the solutions evaluated reaches saturation (SR=1) for the solution at 80 ^{0}C but not for solutions at 50 ^{0}C and 30 ^{0}C. The reason this precipitation occurs at higher temperatures may be that as observed in CO_2 partitioning section, the CO_2 concentration decrease with temperature, the solution will consequently have less alkalinity (buffer capacity) and the a bigger effect on the addition of NaOH is observed.

Also, it is shown that the difference between OLI Studio and MultiScale increases with MEG concentration.

In addition, it is observed that the $Mg(OH)_2$ SR is higher in MultiScale than in OLI Studio. The reason of this difference may be that due to difference in input format, a higher initial concentration of Mg^{2+} was obtain in MultiScale than in OLI Studio.

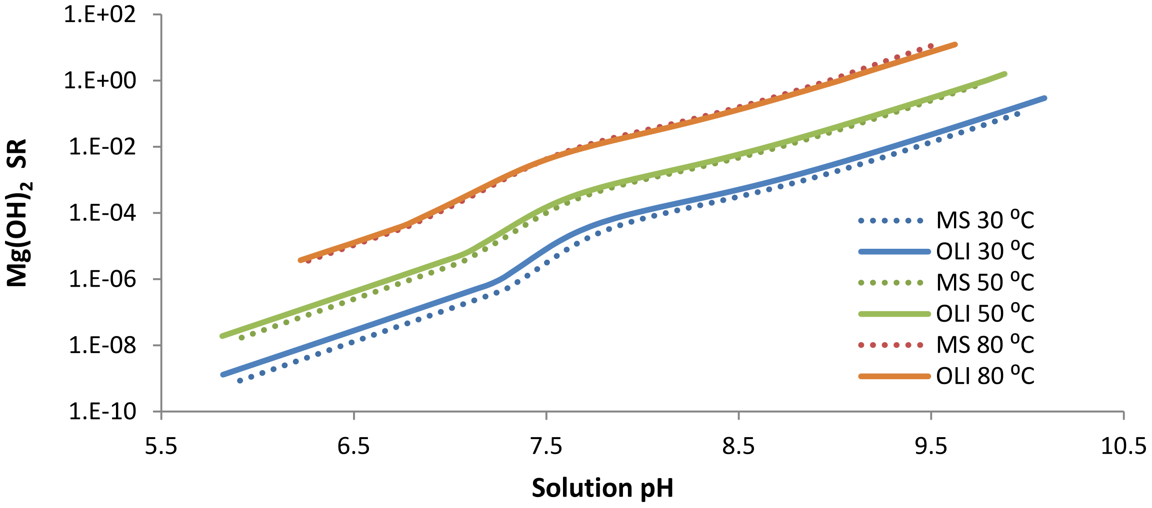

Figure 4-26: $Mg(OH)_2$ SR as function of the solution pH in water solution at 30 ^{0}C, 50 ^{0}C and 80 ^{0}C and 1 bar

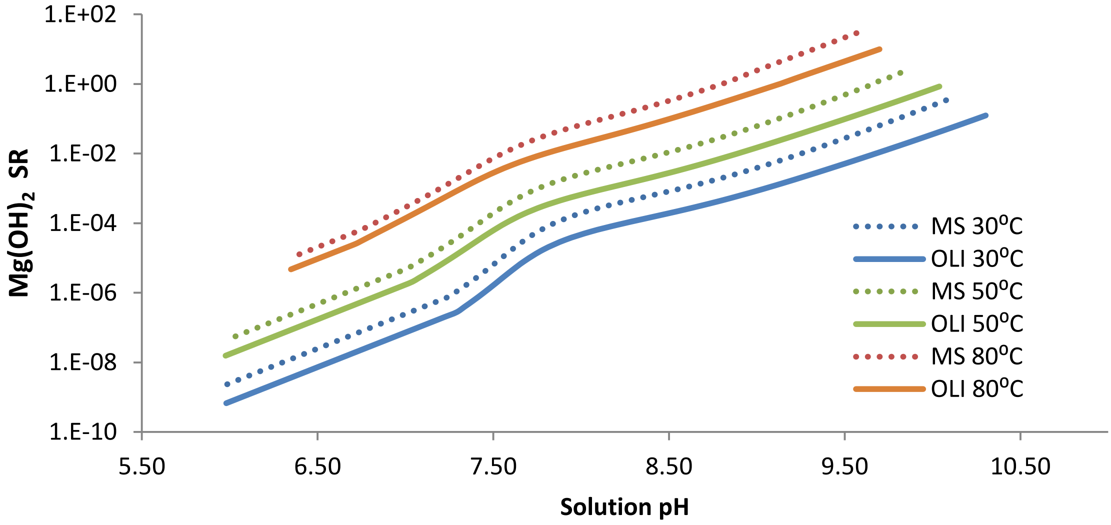

Figure 4-27: $Mg(OH)_2$ SR as function of the solution pH in 20 wt % MEG solution at 30 ^{0}C, 50 ^{0}C and 80 ^{0}C and 1 bar

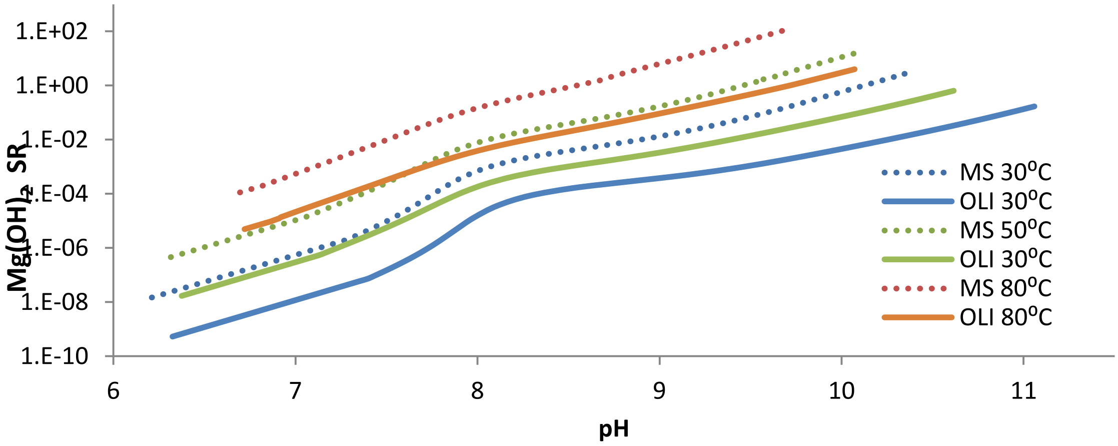

Figure 4-28: $Mg(OH)_2$ SR as function of the solution pH in 50 wt % MEG solution at 30 ºC, 50 ºC and 80 ºC and 1 bar

In order to compare the alkalinity dosing in both software, a reduction of Mg^{2+} concentration to 2 mg/kg of solution has been chosen. Estimation of the alkalinity dosing required to reduce the concentration of Mg^{2+} in water and water-MEG solutions has been calculated and is presented in Figure 4-29. As no precipitation occurs at low temperature, 70 ºC, 80 ºC and 90 ºC has been chosen to observe the discrepancies at different temperatures.

In Figure 4-29 it is shown that the difference between OLI and MultiScale increases with MEG concentration and decreases with temperature. The difference of NaOH concentration in MultiScale and in OLI Studio is from 0.2 mmol/kg to 9.7 mmol/kg. Provided that the flow rate is 100 tons/d, a difference of 9.7 mmol/kg of solution, corresponds to 24.31 kg/d. This difference is considered significant compared to the total dosing required according to OLI Studio which is 48.6 kg/d.

Nevertheless, in water solutions the difference is from 0.2 mmol/kg to 1.1 mmol/kg, as the maximum difference is about 4 %, and taking into consideration that standard typical design margin is minimum 10 %, these differences are not considered significant as it correspond to less than 10 % of the required solution concentration by both software. The correct dosing of NaOH to precipitate the $Mg(OH)_2$ will be cover with the design margin.

These results indicate that there is a considerable difference between OLI Studio and MultiScale in solution containing MEG.

Appendix E, Figure E-28 to Figure E-36 show the Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of the NaOH concentration in water and water-MEG solutions at 70 ºC, 80 ºC and 90 ºC and 1 bar.

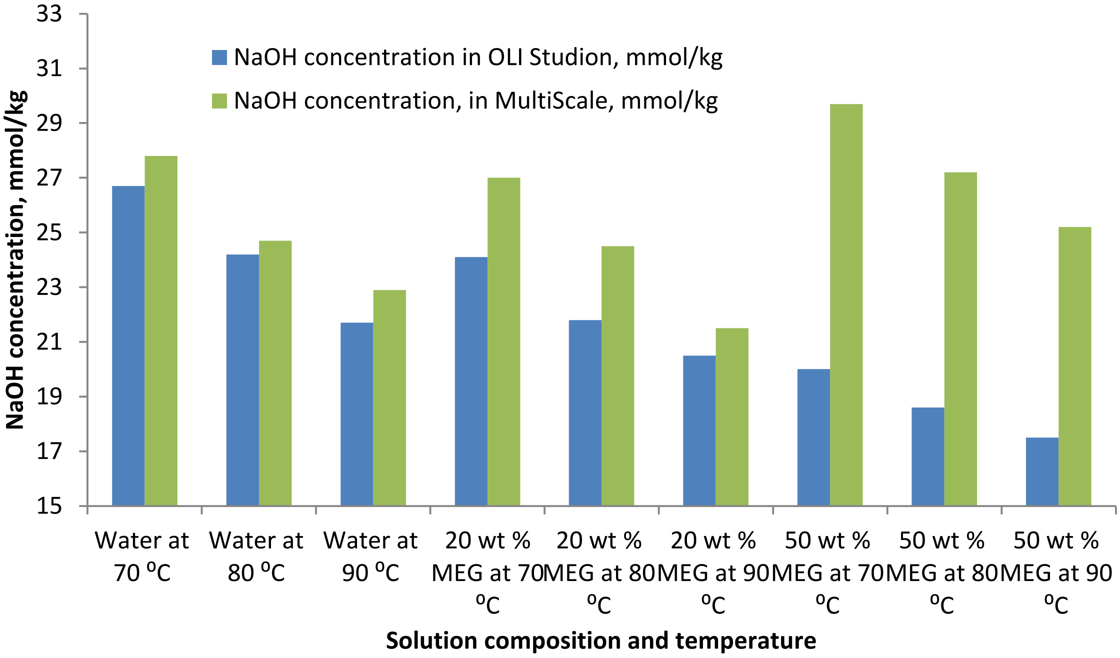

Figure 4-29: NaOH concentration required to decrease the Mg^{2+} concentration from 5mg/kg to 2 mg/Kg in solution in water and water-MEG solutions according to OLI Studio and in MultiScale

These results show that the prediction of the precipitation of low concentrations of Mg^{2+} is considerably different for both software in solution containing MEG.

As correct prediction of pH/alkalinity dosing is required to reduce the Mg^{2+} concentration in the pre-treatment vessel and prevent scale formation. It is recommended that for solution of low concentration of Mg^{2+}, additional approaches should be used to ensure that desired removal of Mg^{2+}. Other approaches include for example, lab test or pilot test.

4.4 Summary

Three sets of evaluations were made in order to compare OLI Studio and MultiScale in the design of a MRU.

The first set consisted of CO_2 partitioning calculations at different conditions of a rich MEG storage tank. These calculations were important to foresee the alkalinity dosing in the pre-treatment section. The results indicated that the discrepancy between OLI Studio and MultiScale increase with the increase of the MEG content and also decrease with the increase of the temperature.

pH is an important parameter which is controlled in the pre-treatment section to precipitate the divalent salt and therefore prevent scale in downstream equipment. Therefore, the second set of evaluation consisted of pH determination using OLI Studio and MultiScale. The calculations consisted of the reproduction of the experimental pH values measured by K. Sandengen. In this section it was observed that the calculated data using OLI Studio and MultiScale corresponded with the experimental data measured by K. Sandengen.

The third set of calculations consisted of a case study where typical MRU design calculations were made at different pressures, temperatures and MEG content. This section showed low discrepancies in the prediction of the precipitation of $CaCO_3$ and high discrepancies in the prediction of the precipitation of $Mg(OH)_2$.

In addition, it was observed discrepancies in the data obtained from OLI Studio and MultiScale due to difference in the input format.

5 Conclusions

A comparison evaluation between OLI Studio and MultiScale™ in the design of a MRU has been done. The main differences between these software have been identified and evaluation has been done based on CO_2 partitioning calculations, pH determination and a case study.

The three main differences identified were:

1) MultiScale™ is developed specifically for prediction of mineral solubility in the presence of MEG, while OLI Studio is develop for prediction of mineral solubility of a wider range of solutions, including mixed organic-water solvents up to saturation.
2) OLI Studio covers thousands of species in water and organic chemical which can be modified by the user. MultiScale™ databank is limited and cannot be modified.
3) OLI Studio can be integrated with a mass and energy balance simulation software. MultiScale™ capabilities do not include integration with a mass and energy balance simulation software.

From the evaluation performed, the following points can be concluded:

1) The difference between OLI Studio and MultiScale™ increased with the increasing content of MEG and decreased with the increased temperature.
2) CO_2 partitioning calculations for water solutions showed a good correspondence in the distribution of the species between OLI Studio and MultiScale™.
3) CO_2 partitioning calculations for water-MEG solutions showed that OLI Studio predicted a lower concentration of dissolved CO_2 than MultiScale™.
4) The OLI Studio reported pH is computed from the H_3O^+ activity and does not include the $HOC_2H_4OH_2^+$ activity (protonated glycol molecule). For pH determination in water-MEG solutions, a different approach based on the concentration-based definition of pH is to be used.
5) No significant difference was found in the comparison of the experimental pH measurement performed by K. Sandengen and the calculated pH from MultiScale™ and OLI Studio (calculated with the concentration-based definition) at a pH range from 5 to 9.
6) Case study calculations showed that pH difference between OLI Studio and MultiScale™ was higher than in previous evaluation, what may be due to salts present in the solution and the difference between scale prediction models in both software. Nevertheless, at pre-treatment operating conditions the pH difference was considered insignificant.
7) The difference between OLI Studio and MultiScale™ was insignificant for the calculations of the precipitation of $CaCO_3$ at the evaluated conditions. The difference between OLI Studio and MultiScale in the calculations of precipitation of $Mg(OH)_2$ showed a notable for solutions containing MEG.
8) OLI Studio has proven to have more flexibility and capabilities than MultiScale. Also both models agreed in the determination of solution pH and in the conditions required to precipitate $CaCO_3$ at the conditions evaluated. However, there is a remarkable difference between OLI Studio and MultiScale in the prediction of precipitation of $Mg(OH)_2$ which doesn't comply with *Fjords Processing* experience. For this reason, MultiScale simulation

software seems to provide more reliable results than OLI Studio. More tests and evaluations are required before start using OLI Studio.

6 Recommendation

1) A comparison between OLI Studio and MultiScale™ can be done to the whole MRU loop, to compare the salts behaviour and accumulation in the system while reaching steady state.
2) An evaluation of the OLI Studio integration with a mass and energy simulation software should be done to ensure consistency in the results.
3) A comparison between OLI Studio and MultiScale™ can be done for the design of the reclamation section to observe the difference between these models in the prediction of the precipitation of high solubility salts.
4) The significant difference was found between OLI Studio and MultiScale™ at low pH and at low concentrations of Mg^{2+}, these results can be compared with lab test or pilot test to identify which software provide more reliable results at this conditions.
5) Reported pH in OLI Studio does not include the effect of MEG. For this reason, further investigation should be done to identify how to implement the pH as input in OLI in solution containing MEG.

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Appendices

Appendix A OLI Modern Formulations

Table A-1 Modern formulations included in the OLI framewor [8]

	Formula	**Description of parameters**
Bromley – Zematis	$Log\ \gamma_{\pm} = \frac{-A\lvert Z_{+}Z_{-}\rvert\sqrt{I}}{1+\sqrt{I}} + \frac{(0.06+0.06B)}{\left(1+\frac{1.5I}{\lvert Z_{+}Z_{-}\rvert}\right)} + BI + CI^{2} + D^{3}$	A = Debye-Huckel Constant I = Ionic Strength B = Bromley parameter γ = Mean activity coefficient Z+ = Charge of the cation Z- = Charge of the anion
Pitzer	$\ln \gamma_{\pm} = \lvert Z_{+}Z_{-}\rvert f^{\gamma} + m\left(\frac{2(v_{+}v_{-})}{v}\right)B_{\pm}^{\gamma} + m^{2}\left(\frac{2(v_{+}v_{-})}{v}\right)C_{\pm}^{\gamma}$	f^{γ}= The “Debye-Huckel” term. $v_{+}v_{-}$= Stoichiometric coefficient for the cation and anion ν = ν+ + ν- m = Concentration in molal $B_{\pm}^{\gamma}$= Pitzer B term, containing the adjustable parameters $C_{\pm}^{\gamma}$= Pitzer C term, containing adjustable parameters
Helgeson	$\log \overline{\gamma_{\pm}} = \frac{-A_{\gamma}}{1+a_{0}B_{\gamma}\sqrt{\bar{I}}} + \Gamma_{\gamma} + \left(\frac{\omega_{k}}{v_{k}}\sum_{k} b_{k}\, Y_{k}\bar{I} + \frac{v_{i,k}}{v_{k}}\sum_{l}\frac{b_{il}\overline{Y_{l}}\sqrt{\bar{I}}}{\psi_{l}} + \frac{v_{l,k}}{v_{k}}\sum_{i}\frac{b_{il}\overline{Y_{i}}\sqrt{\bar{I}}}{\psi_{i}}\right)$	A_{γ} = Debye-Huckel constant according to Helgeson Z_{γ} = Charge of the cation Z_{l} = Charge of the cation a_{0} = ion size parameter B_{γ} = Extended Debye-Huckel term according to Helgeson $\bar{I}$ = True ionic strength which includes the effects of complexation. Γ_{γ} = Conversion of molal activity to mole fraction activity ω_{k} =Electrostatic effects on the solvent due to the species k v_{k} = moles of electrolyte (summation) $v_{i,k}$ = moles of cation per mole of electrolyte $v_{l,k}$ = moles of anion per mole of electrolyte b_{il} = adjustable parameter for the ion-ion interaction $\overline{Y}_{i}$ = fraction of ionic strength on a true basis attributed to the cation $\overline{Y}_{l}$ = fraction of ionic strength on a true basis attributed to the anion ψ_{i} = ½ the cation charge ψ_{l} = ½ the anion charge Z_{i} = the cation charge Z_{l} = the anion charge

Appendix B MultiScale Report

```
MultiScale 8.1   Result file
 Type: Single Point
 Date: 04.03.2016
 Time: 14:39

 ***  WATER INPUT ANALYSES ***
  Water analysis:
 C:\Data_TempFilesOnly\MultiScale\Water analyses\Sandengen table 4.15.wat
---------------------------------------------------------------
                    CONCENTRATION
  ION          mmol/kgSolvent    mg/kgSolvent
---------------------------------------------------------------
  Na+       :      19.90    |      457.50
  K+        :      0.00    |       0.00
  Mg2+      :       0.00    |       0.00
  Ca2+      :       0.00    |       0.00
  Ba2+      :       0.00    |       0.00
  Sr2+      :       0.00    |       0.00
  Fe2+      :       0.00    |       0.00
  Cl-       :      0.00    |       0.00
  Br-       :      0.00    |       0.00
  SO42-     :       0.00    |       0.00
---------------------------------------------------------------
  Formic acid :       0.00    |       0.00
  Acetic acid :       0.00    |       0.00
  Prop acid   :       0.00    |       0.00
  But acid    :       0.00    |       0.00
  Alkalinity  :      19.90    |     1214.26
  Density will be estimated
---------------------------------------------------------------
  MEG concentration:  60.0000 Wt%   relative to solution
---------------------------------------------------------------
 Water analysis data:
  Pressure     :     1.00 bar
  Temperature  :     25.00 C
  GWR          :    0.00 m3/m3
 Gas concentrations in water:
  CO2       :   19.90 mmol/kgSolvent
  H2S       :    0.00 mmol/kgSolvent
  CH4       :    0.00 mmol/kgSolvent
---------------------------------------------------------------


 ***  OIL AND GAS INPUT ANALYSES ***

 PVTFILE:
 C:\Data_TempFilesOnly\MultiScale\Oil and gas analyses\CO2.oil
```

```
------------------------------------------------------------
 Name : CO2
 Field:
 Well :
 Fluid:
 Text :
------------------------------------------------------------
 COMPOSITION
------------------------------------------------------------
 KOMP       MOLE(%)    MW(g/mole)  DENSITY(kg/m3)
------------------------------------------------------------
 CO2       100.000     44.010      0.000
------------------------------------------------------------

 Flash at :  Pressure   :       0.98 bar
          Temperature:      25.00 C
------------------------------------------------------------
 PROPERTIES      TOT       OIL       GAS       Aqueous
------------------------------------------------------------
 Volume    :   100.0000     0.0000   100.0000     0.0000 m3
 Vol%     :   100.0000     0.0000   100.0000     0.0000 %
 Mole%    :   100.0000     0.0000   100.0000     0.0000 %
 Density  :      1.7483     0.0000      1.7483     0.0000 kg/m3
 Z-factor  :     0.9951     0.0000     0.9951     0.0000
 Moleweight:    44.0100     0.0000    44.0100     0.0000 g/mole
------------------------------------------------------------
*****************************************************
*                                           *
*       RESULTS                                   *
*                                           *
*****************************************************

 Pressure:               1.01 bar
 Temperature:           25.00 C

  WATERS:
------------------------
 NO  RATE[m3/d] NAME/PATH
 1      100.0  C:\Data_TempFilesOnly\MultiScale\Water analyses\Sandengen table 4.15.wat

 GASES:
------------------------
 NO  RATE[m3/d] NAME/PATH
 1      100.0  C:\Data_TempFilesOnly\MultiScale\Oil and gas analyses\CO2.oil


GENERAL INFO           Initial      Equilbrium
----------------------------------------------------------------------
 pH                   6.6055       6.6055
 Water activity         0.6944       0.6944
 MEG mole fraction       0.3042       0.3042
 MEG wt% rel water      60.1008      60.1008
```

```
 Tot CO2 in aq        43.9707     43.9707  mmol/kgSolvent
 Tot H2S in aq         0.0000      0.0000  mmol/kgSolvent
 Tot CH4 in aq         0.0000      0.0000  mmol/kgSolvent
 Alkalinity EN        19.9002     19.9002  mmol/kgSolvent
 Ionic strength        0.0199      0.0199   mol/kgSolvent
 Charge              0.0000      0.0000  mmol/kgSolvent
 Dissovled species    2731.1059    2731.1059    mg/kgSolvent
 Density              1.0640      1.0640    kg/l
----------------------------------------------------------------------


WATER COMPOSITION  (mmol/kgSolvent)
----------------------------------------------------------------------
 Ion        Initial          Equilibrium
----------------------------------------------------------------------
 H+         2.5339E-04        2.5339E-04
 OH-        1.0815E-04        1.0815E-04
 Na+        1.9900E+01        1.9900E+01
 CO2        2.4071E+01        2.4071E+01
 HCO3-      1.9898E+01        1.9898E+01
 CO32-      9.4402E-04        9.4402E-04
----------------------------------------------------------------------
  *Only species with concentration > zero are written
  *Activity coefficients are not available when MEG is present


SATURATION RATIO AND PRECIPITATION
----------------------------------------------------------------------
 Salt       Init SR       Precipitation        Eq SR
                     mmol/kg    kg/day
----------------------------------------------------------------------
 NaHCO3      0.0041      0.0000      0.0000      0.0041
----------------------------------------------------------------------
  *Only salts with SR higher than 0.0001 are shown


COMPOSITION AND FUGACITY COEFFISIENTS OF OIL AND GAS PHASE
----------------------------------------------------------------------
 Component   Total   |       Oil         |       Gas
         mol%    |  mol%    FugCoef  |  mol%     FugCoef
----------------------------------------------------------------------
  MEG       0.0037  |   0.0000    1.0000  |   0.0037    0.9774
  H2O       2.1831  |   0.0000    1.0000  |   2.1831    0.9889
  CO2      97.8132  |   0.0000    1.0000  |  97.8132    0.9950
----------------------------------------------------------------------


PHASE DISTRIBUTION
----------------------------------------------------------------------
          Mass rate |          Phase distribution (%)
           kg/day   |    Oil      Gas       Aqueous   Solids
----------------------------------------------------------------------
```

```
  MEG       63795.27  |     0.000     0.000   100.000     0.000
  H2O       42390.51  |     0.000     0.001    99.999     0.000
  CO2         267.80  |     0.000    23.296    76.704     0.000
----------------------------------------------------------------------
Water and MEG in the hydrocarbon phase quals approx:      0.00 m3/d


PHASE PROPERTIES
----------------------------------------------------------------------
 Property           Total       Oil        Gas        Aqueous
----------------------------------------------------------------------
  Volume           135.2952      0.0000     35.2642     100.0310   m3/day
  Z-Factor           0.0016      0.0000      0.9948      0.0012
  Density          786.8261      0.0000      1.7853    1064.0407  kg/m3
  Avg moleweight     31.4321      0.0000     43.4432     31.4402  g/mole
  Enthalpy       -50883.7697      0.0000    872.0586  -50905.9529  J/mole
  Entropy          -121.5345      0.0000      3.9781    -121.5883  J/mole K
  Cp               112.6828      0.0000     37.3174     112.7151  J/mole K
  Cv                89.3754      0.0000     28.8102      89.4013  J/mole K
  JT                 0.0000      0.0000      1.0941      -0.0259  K/bar
----------------------------------------------------------------------

 VOLUMETRIC RELATIONS
----------------------------------------------------------------------
  GOR       0.0000    m3 gas/m3 oil
  GWR       0.3525    m3 gas/m3 wat
  GLR       0.3525    m3 gas/m3 liquid
  GFR      26.0646    Vol% of gas
  WCUT    100.0000    Vol%
----------------------------------------------------------------------

 EQUILIBRIUM CONSTANTS
----------------------------------------------------------------------
 EqName     EqTerm        GammaPitz      GammaMEG       EqStok
----------------------------------------------------------------------
 KspFeCO3    4.2724291E-11  4.8951144E-01  5.5771606E+00  1.5649442E-11
 KspCaCO3c   3.1998387E-09  3.0763116E-01  5.5771606E+00  1.8650248E-09
 KspCaCO3a   4.3989665E-09  3.0763116E-01  5.5771606E+00  2.5639360E-09
 KspCaCO3v   1.1498872E-08  3.0763116E-01  5.5771606E+00  6.7021136E-09
 KspBaSO4    1.1616867E-10  2.9634153E-01  1.3033299E+01  3.0077528E-11
 KspSrSO4    2.4753765E-07  2.9615281E-01  3.8090665E+01  2.1943548E-08
 KspCaSO4A   4.1318299E-05  3.0245288E-01  3.1327689E+01  4.3607014E-06
 KspCaSO4G   2.6392526E-05  3.0177666E-01  1.9798197E+01  4.4174298E-06
 KHCO2       3.3633148E-02  1.0082367E+00  1.3738065E+00  2.4281721E-02
 K1CO2       4.3272541E-07  7.4303220E-01  2.7803775E+00  2.0945995E-07
 K2CO2       4.6854169E-11  5.5922235E-01  6.9697839E+00  1.2021106E-11
 KassCaCO3   1.6298948E+03  3.2506460E+00  1.7930271E-01  2.7964241E+03
 KHAc        1.7431004E-05  7.5482692E-01  6.4815404E+00  3.5628437E-06
 Kw          1.0581205E-14  7.5338212E-01  5.1250259E-01  2.7404618E-14
 KassCaHCO3  1.2257944E+01  1.8159704E+00  1.1008138E+00  0.0000000E+00
```

```
KassHSO4    9.7330112E+01  1.8409873E+00  8.8086164E-01  6.0018998E+01
KHCH4       1.3712798E-03  1.0050126E+00  1.1778854E+00  1.1583814E-03
KassCaSO4   1.0000000E+00  3.3063001E+00  2.5748783E+00  1.1746298E-01
KHH2S       1.0178165E-01  1.0072467E+00  1.0392472E+00  9.7233243E-02
K1H2S       1.0095980E-07  7.6043178E-01  1.5469748E+00  8.5823257E-08
KspCaSO4H   2.4752340E-04  3.0228368E-01  2.1797432E+01  3.7566110E-05
KspNaCl     3.8871395E+01  7.5719435E-01  1.2637571E+01  4.0621798E+00
KspFeS      2.4596615E-04  8.9518804E-01  1.0000000E+00  2.7476479E-04
KspKCl      8.2099409E+00  7.5423578E-01  8.7363234E+00  1.2459603E+00
KHFormic    1.7643085E-04  7.4256820E-01  1.8795132E-01  1.2641331E-03
KHProp      1.3363505E-05  7.4256820E-01  1.8795132E-01  9.5749971E-05
KHBut       1.5514833E-05  7.4257005E-01  1.8795132E-01  1.1116403E-04
KspHydroMg  1.7982836E-32  1.2628697E-02  2.5301338E+03  5.6280269E-34
KspBaCO3    3.0549007E-09  3.0141518E-01  5.0491956E+00  2.0072884E-09
KspSrCO3    6.4862307E-10  3.0122322E-01  5.8873887E+00  3.6574739E-10
KspNaHCO3   3.9909687E-01  7.4871407E-01  5.4638285E+00  9.7558535E-02
KspKHCO3    1.5410450E+00  7.4578864E-01  5.2894688E+00  3.9064970E-01
KspNa2CO3D  1.7165631E-01  4.1633856E-01  1.9969240E+00  2.0646746E-01
KspNa2CO3M  5.3242472E+00  4.2055322E-01  1.3756742E+02  9.2028356E-02
KspK2CO3H   8.0532031E+02  4.1703978E-01  1.9991065E+02  9.6595134E+00
KspK2CO3A   5.5890999E+12  4.1774046E-01  3.4488730E+02  3.8793426E+10
KspNaAcT    3.3475207E+01  7.5647706E-01  2.5163066E+00  1.7585874E+01
KspNaAcA    1.5698257E+03  7.5902114E-01  3.6178163E+00  5.7167745E+02
KHHFormic   8.8109159E+03  1.0208775E+00  1.5987319E+00  5.3984837E+03
KHHAc       3.7274836E+03  1.0234771E+00  1.5987319E+00  2.2780433E+03
KHHProp     5.5826011E+03  1.0266341E+00  1.5987319E+00  3.4013027E+03
KHHBut      4.7270000E+03  1.0301325E+00  1.5987319E+00  2.8702311E+03
KspMgOH2    9.8201867E-12  4.2254946E-01  1.0000000E+00  2.3240325E-11
KspNa2CO3A  4.8004263E+01  4.2102415E-01  1.2776991E+02  8.9236850E-01
Kamin       1.0000000E-09  1.0000000E+00  1.0000000E+00  1.0000000E-09
```

Appendix C Results from CO_2 Partitioning

Water with and without alkalinity at 1 bar:

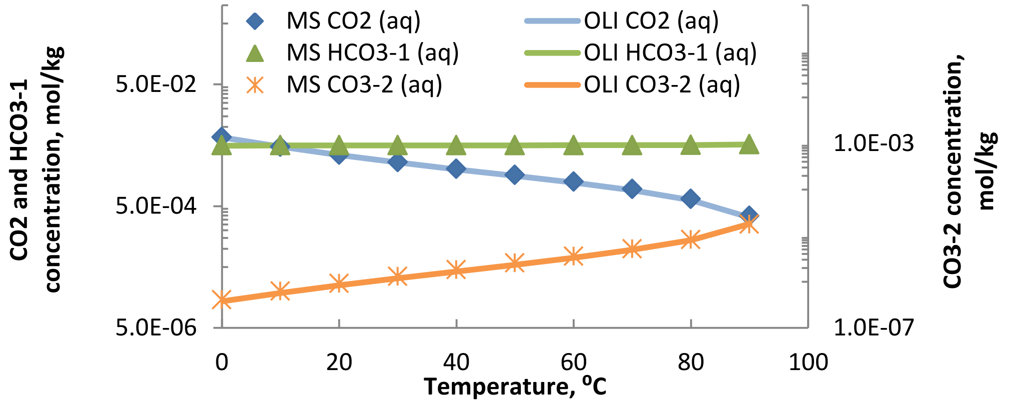

Figure C-1: Dissolved CO_2, HCO_3^- and CO_3^{-2} in water as a function of temperature at 1 bar. CO_2 content in the gas phase is 10 mole%

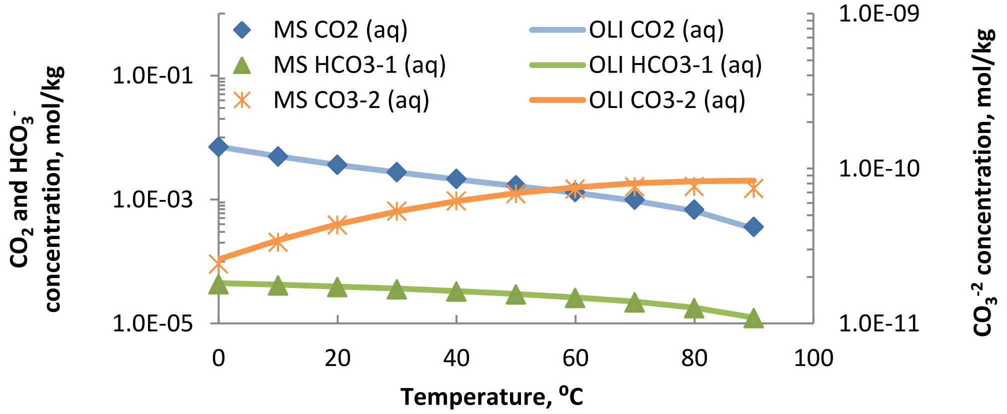

Figure C-2: Dissolved CO_2, HCO_3^- and CO_3^{2-} in water with NaOH as a function of temperature at 1 bar. CO_2 content in the gas phase is 10 mol %

50 wt % MEG with and without alkalinity at 1 bar

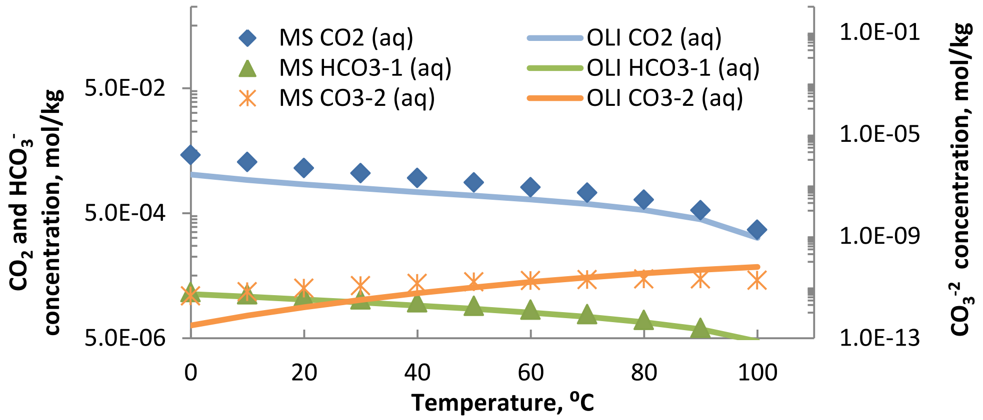

Figure C-3: Dissolved CO_2, HCO_3^- and CO_3^{-2} in a solution of 50 wt % MEG as a function of temperature at 1 bar. CO_2 content in the gas phase is 10 mol %

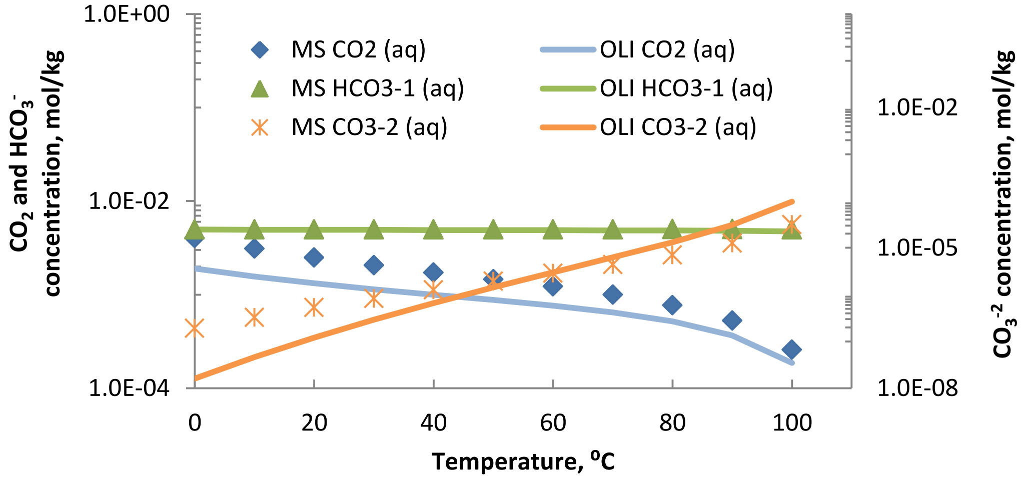

Figure C-4: Dissolved CO_2, HCO_3^- and CO_3^{-2} in a solution of 50 wt % MEG with NaOH as a function of temperature at 1 bar. CO_2 content in the gas phase is 10 mol %

Results for water with and without alkalinity at 10 bar:

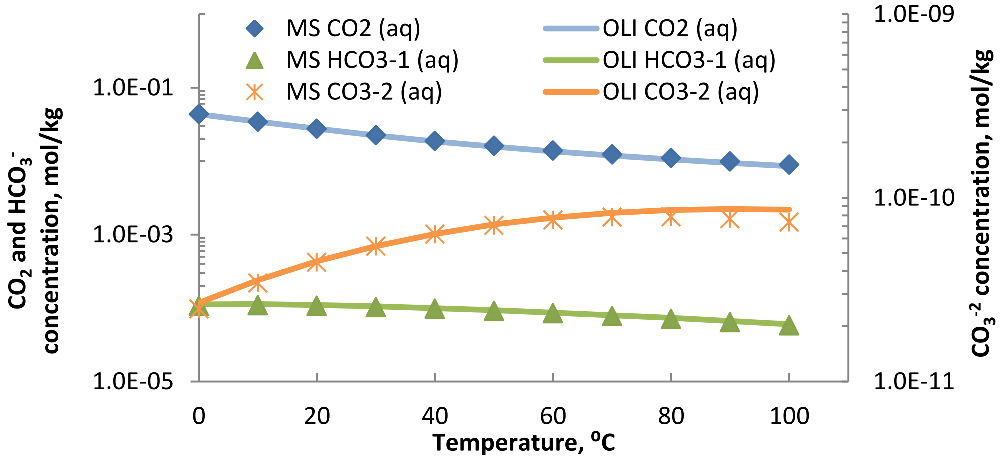

Figure C-5: Dissolved CO_2, HCO_3^- and CO_3^{-2} in water with NaOH as a function of temperature at 10 bar. CO_2 content in the gas phase is 10 mol %

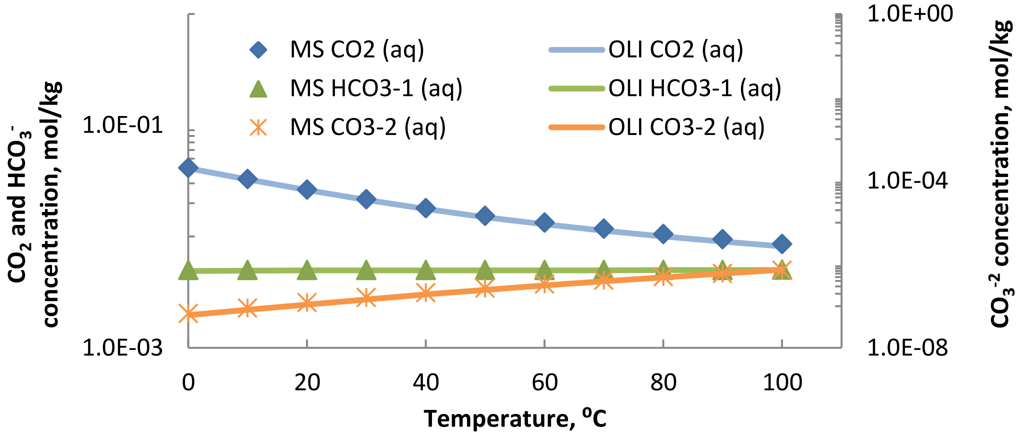

Figure C-6: Dissolved CO_2, HCO_3^- and CO_3^{-2} in water without NaOH as a function of temperature at 10 bar. CO_2 content in the gas phase is 10 mol %

Results for 50 wt % MEG with and without alkalinity at 10 bar:

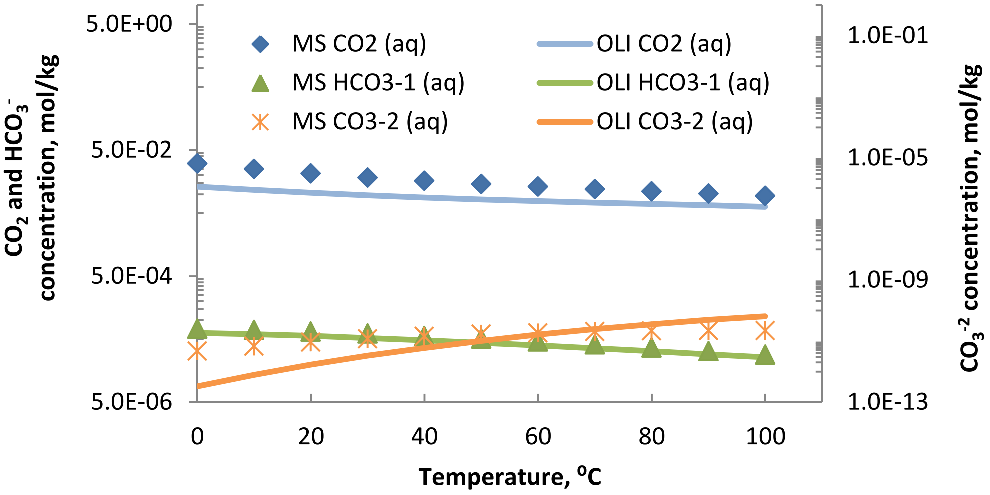

Figure C-7: Dissolved CO_2, HCO_3^{-1} and CO_3^{-2} in a solution of 50 wt % MEG as a function of temperature at 10 bar. CO_2 content in the gas phase is 10 mol %

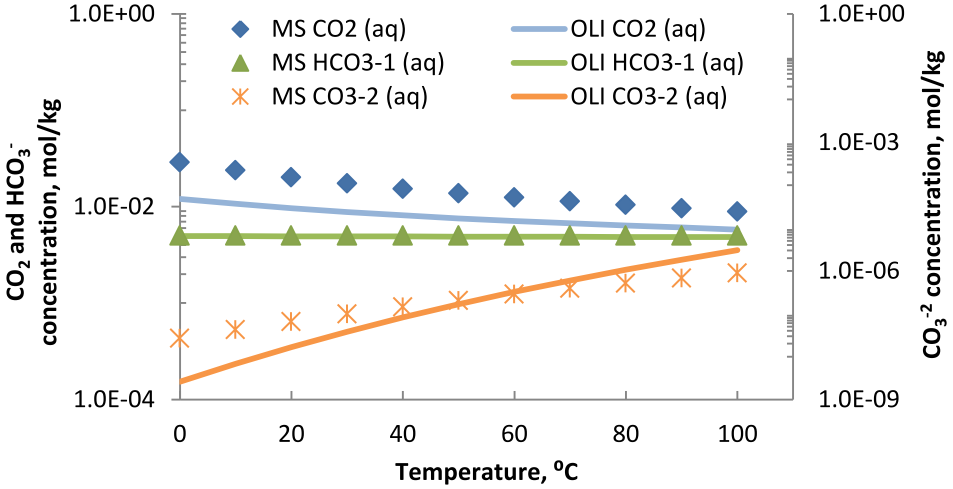

Figure C-8: Dissolved CO_2, HCO_3^{-1} and CO_3^{-2} in a solution of 50 wt % MEG with NaOH as a function of temperature at 10 bar. CO_2 content in the gas phase is 10 mol %

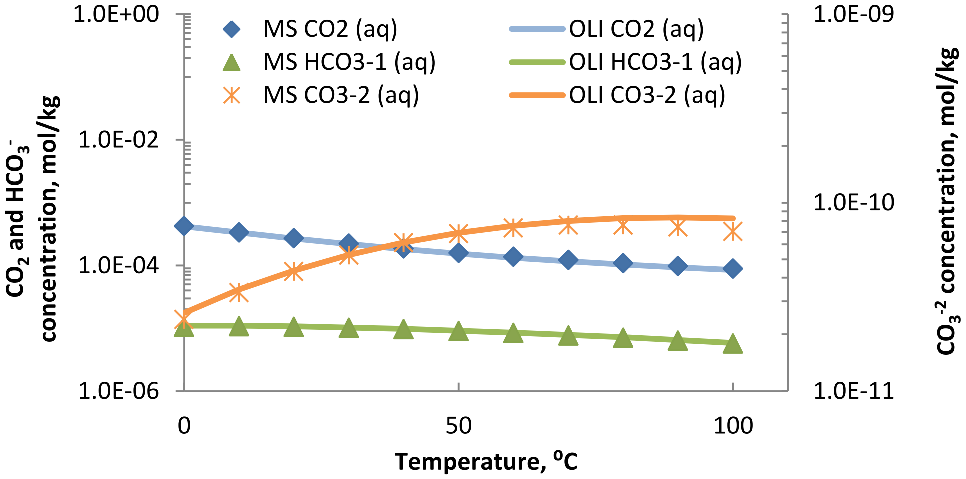

Figure C-9: Dissolved CO_2, HCO_3^- and CO_3^{-2} in water with NaOH as a function of temperature at 10 bar. CO_2 content in the gas phase is 0.1 mol %

Appendix D Results from pH determination

Table D-2: pH data obtained from K. Sandengen and the calculated data with MultiScale at 60% MEG and 25^{o}C

mmol/kg solvent	Experimental pH measured by K. Sandengen) [7]	Calculated pH from MultiScale	Difference between experimental pH and pH from MultiScale
0	4.13	4.14	0.01
19.9	6.58	6.60	0.02
99.4	7.21	7.24	0.03
199	7.49	7.51	0.02
298.9	7.65	7.66	0.01
399.5	7.77	7.77	0.00
599	7.8	7.93	0.13

Table D-3: pH data obtained from K. Sandengen and the calculated data with MultiScale at 60 % MEG and 80 ^{o}C

mmol/kg solvent	Experimental pH measured by K. Sandengen) [7]	Calculated pH from MultiScale	Difference between experimental pH and pH from MultiScale
0	4.88	4.18	0.70
1	5.9	5.83	0.06
9	6.8	6.76	0.04
47	7.45	7.43	0.02
104.3	7.82	7.75	0.07
164.1	7.96	7.92	0.04
216.9	8.1	8.03	0.07
270.2	8.2	8.11	0.09
313.1	8.22	8.17	0.05
378.5	8.29	8.24	0.05
514.1	8.3	8.25	0.05

Table D-4: pH data obtained from K. Sandengen and the calculated data with MultiScale at 90 % MEG and 25 ^{o}C

mmol/kg solvent	Experimental pH measured by K. Sandengen) [7]	Calculated pH from MultiScale	Difference between experimental pH and pH from MultiScale
0	4.76	4.49	0.27
1	6.69	6.62	0.07
9	7.21	7.13	0.08
47	7.81	7.74	0.07
104.3	8.04	7.99	0.05
164.1	8.37	8.30	0.07
216.9	8.47	8.43	0.04

Table D-5: pH data obtained from K. Sandengen and the calculated data with MultiScale at 90 % MEG and 80 ^oC

mmol/kg solvent	Experimental pH measured by K. Sandengen) **[7]**	Calculated pH from MultiScale	Difference between experimental pH and pH from MultiScale
0	5.4	4.54	0.86
0.96	6.59	6.53	0.06
8.8	7.53	7.46	0.07
46.1	8.16	8.13	0.03
92.9	8.34	8.40	0.06
180.56	8.59	8.65	0.06
297.2	8.74	8.84	0.1
452.2	8.88	8.99	0.11

Results for water

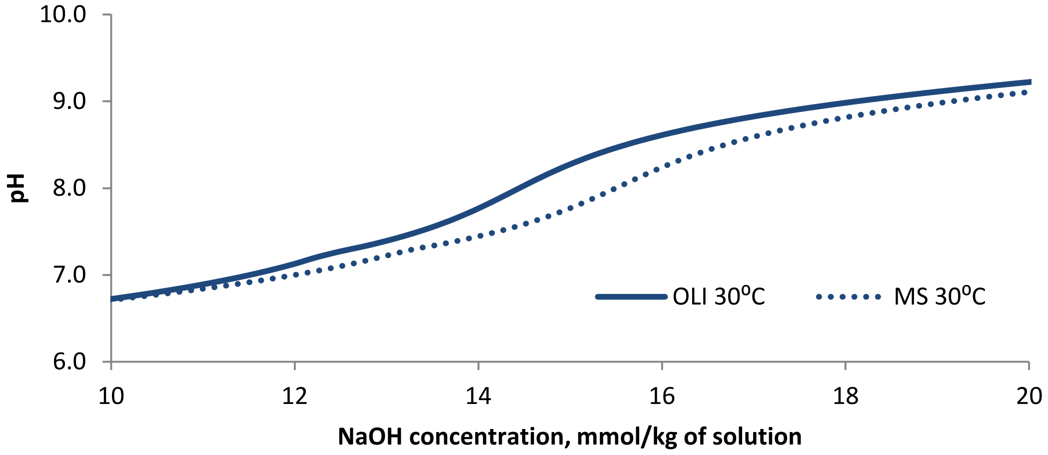

Figure D-10: pH as function of NaOH concentration in water at 30 ^oC and 1 bar

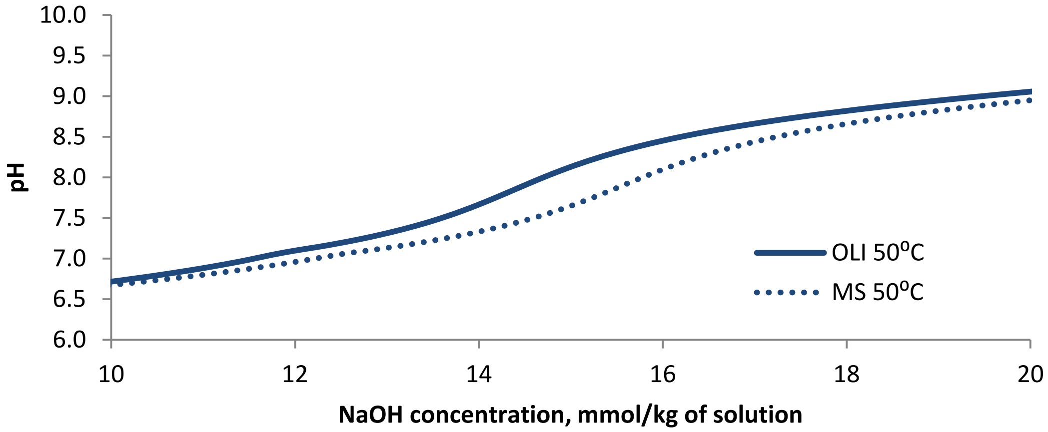

Figure D-11: pH as function of NaOH concentration in water at 50 ^oC and 1 bar

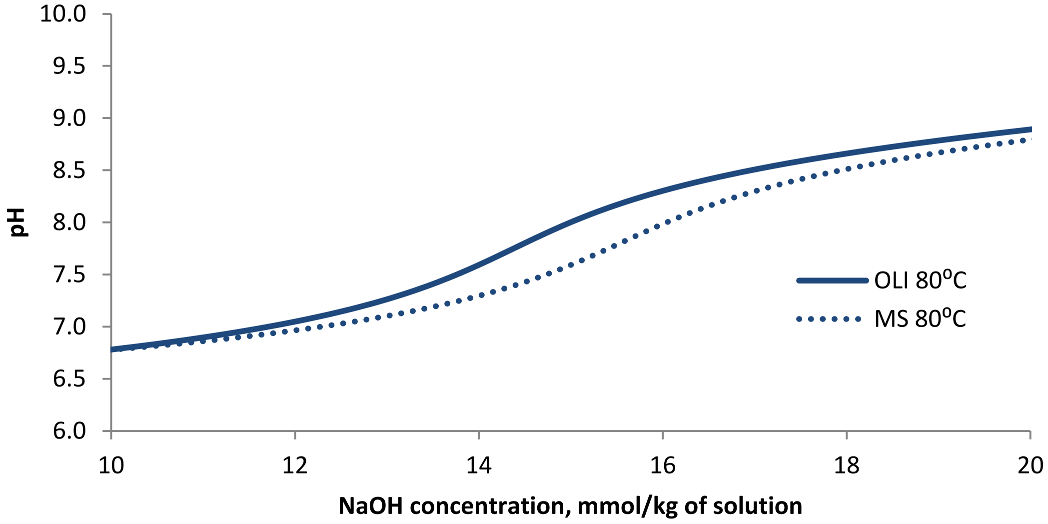

Figure D-12: pH as function of NaOH concentration in water at 80 °C and 1 bar

Results for 20 wt % MEG

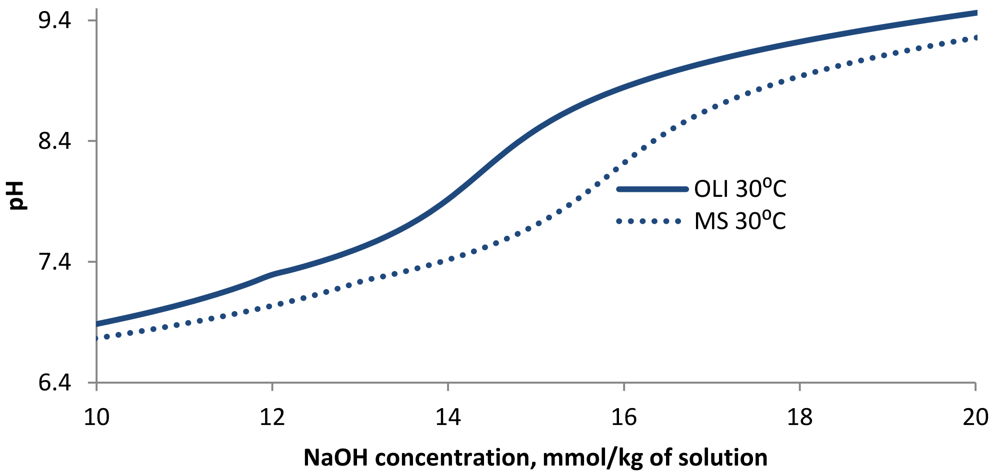

Figure D-13: pH as function of NaOH concentration in 20 wt % MEG solution at 30 °C and 1 bar

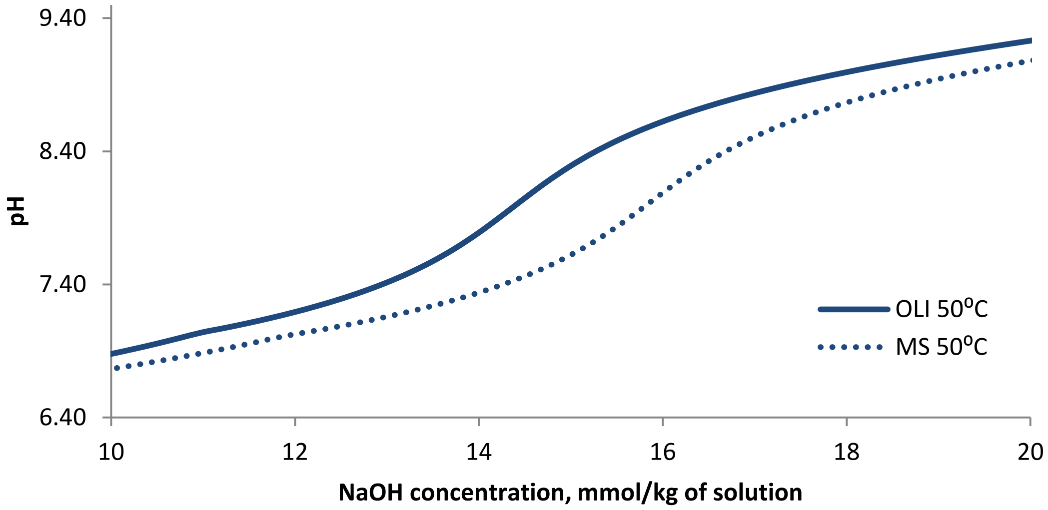

Figure D-14: pH as function of NaOH concentration in 20 wt % MEG solution at 50 °C and 1 bar

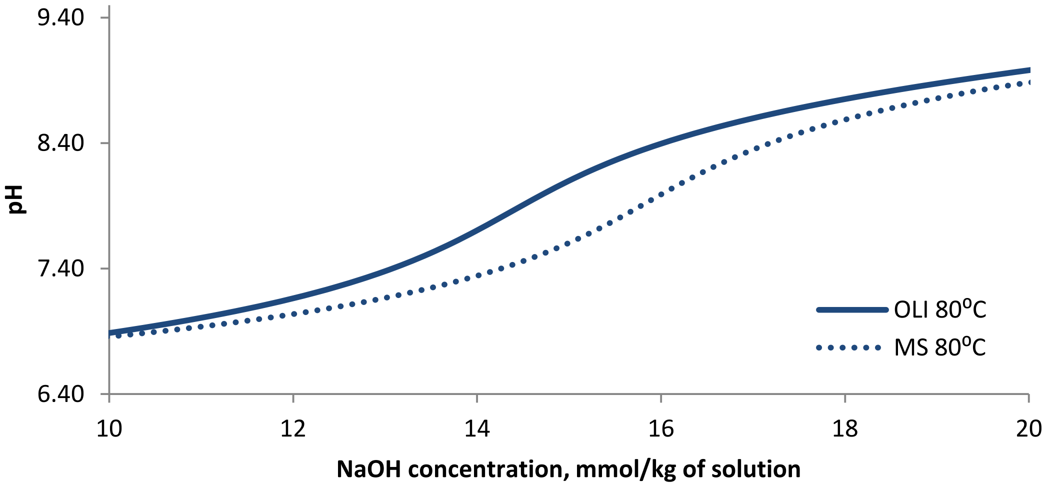

Figure D-15: pH as function of NaOH concentration in 20 wt % MEG solution at 80 °C and 1 bar

Results for 50 wt % MEG

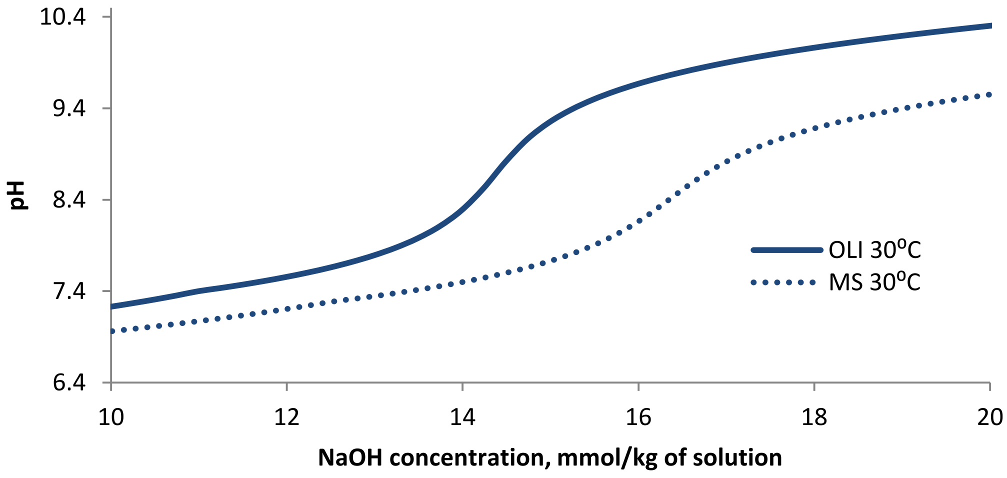

Figure D-16: pH as function of NaOH concentration in 50 wt % MEG solution at 30 °C and 1 bar

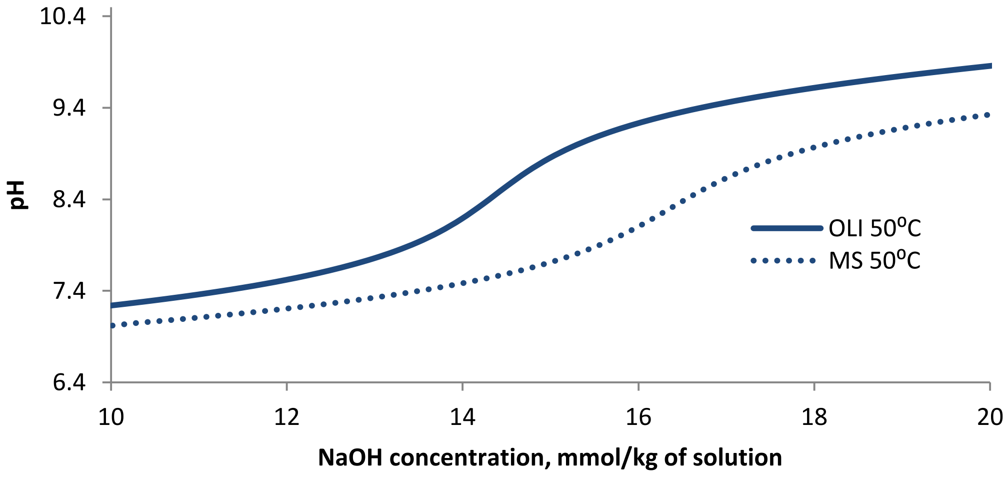

Figure D-17: pH as function of NaOH concentration in 50 wt % MEG solution at 50 °C and 1 bar

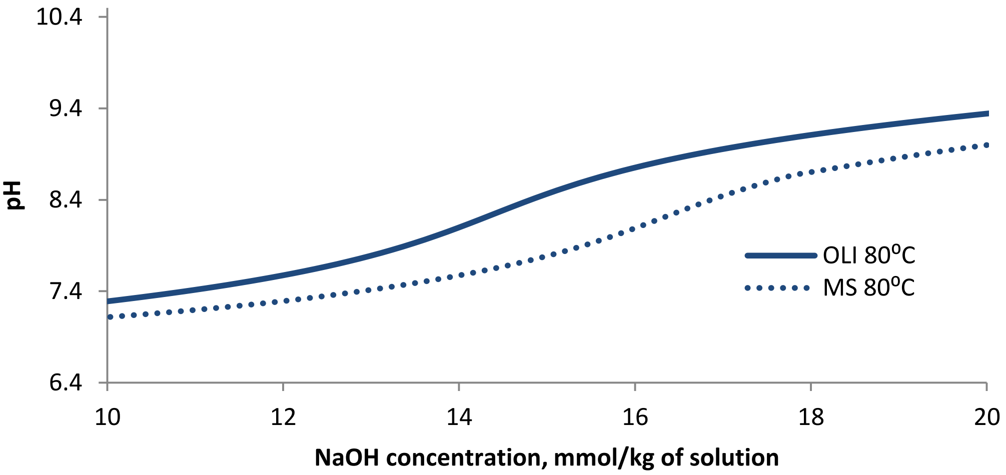

Figure D-18: pH as function of NaOH concentration in 50 wt % MEG solution at 80 ^{o}C and 1 bar

Appendix E Results from Case Study

Calcium ions

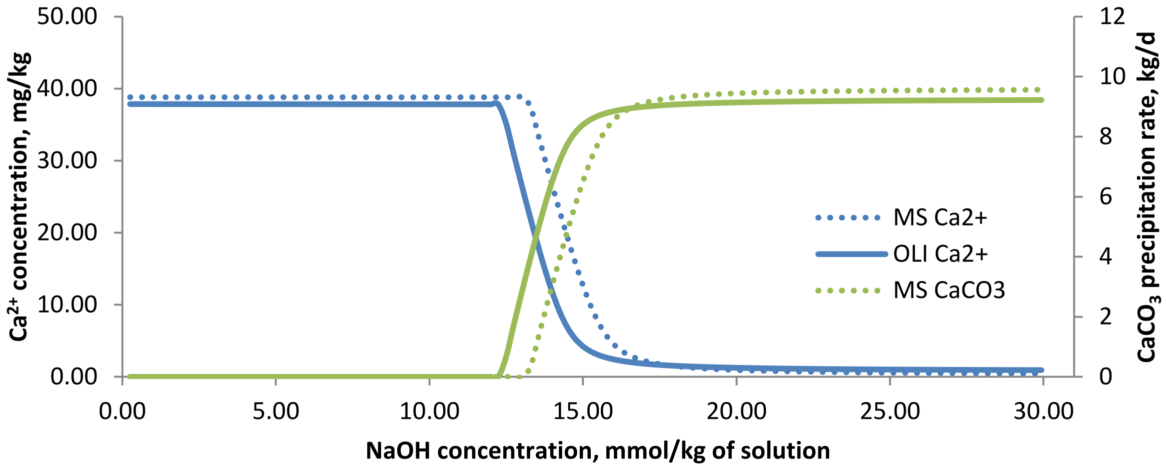

Figure E-19: Ca^{2+} concentration and $CaCO_3$ precipitation rate as function of NaOH concentration in water at 30 °C and 1 bar

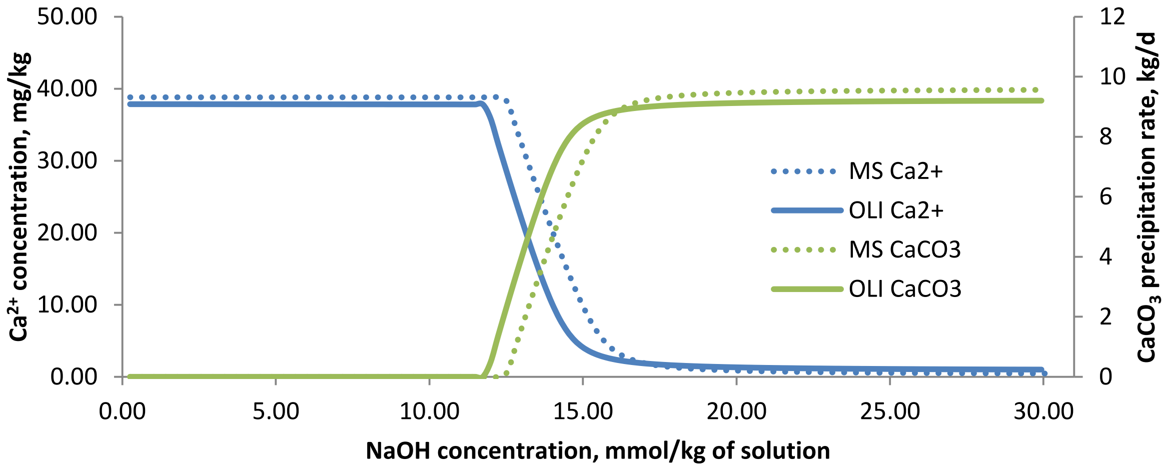

Figure E-20: Ca^{2+} concentration and $CaCO_3$ precipitation rate as function of NaOH concentration in water at 50 °C and 1 bar

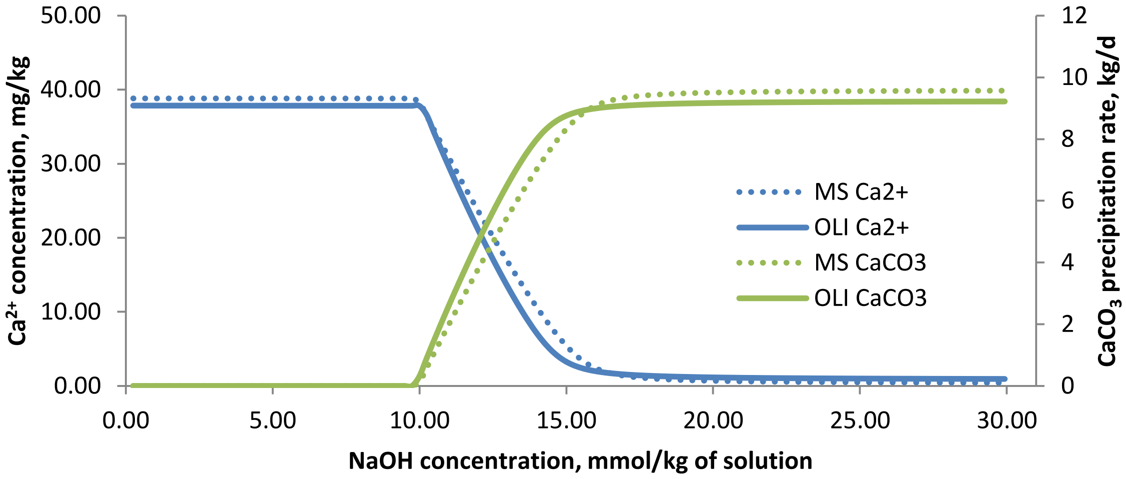

Figure E-21: Ca^{2+} concentration and $CaCO_3$ precipitation rate as function of NaOH concentration in water at 80 °C and 1 bar

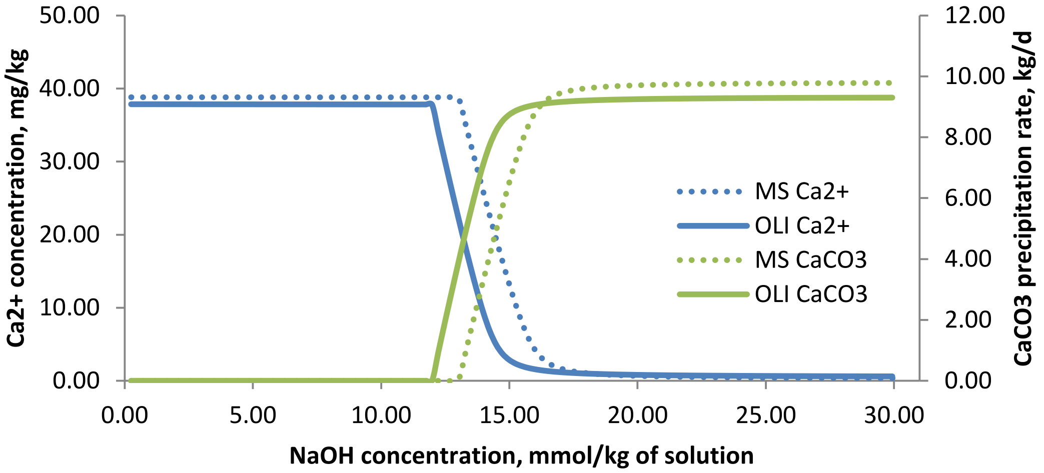

Figure E-22: Ca^{2+} concentration and CaCO$_3$ precipitation rate as function of NaOH concentration 20 wt % MEG at 30 ^{o}C and 1 bar

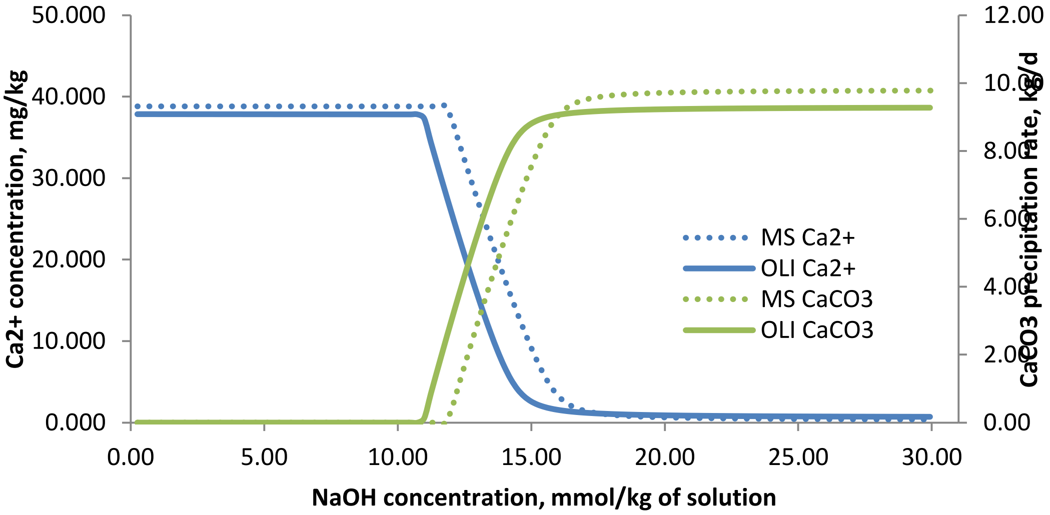

Figure E-23: Ca^{2+} concentration and CaCO$_3$ precipitation rate as function of NaOH concentration in 20 wt % MEG solution at 50 ^{o}C and 1 bar

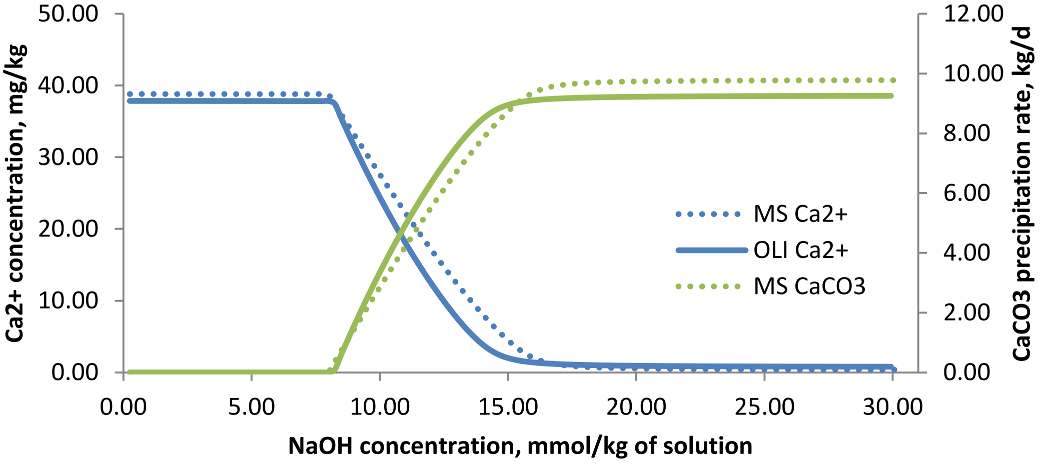

Figure E-24: Ca^{2+} concentration and CaCO$_3$ precipitation rate as function of NaOH concentration 20 wt % MEG at 80 ^{o}C and 1 bar

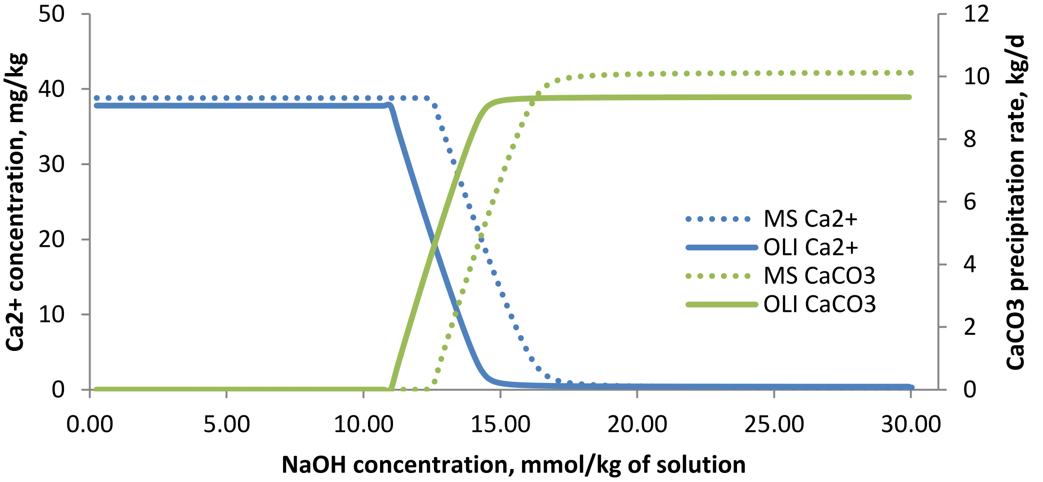

Figure E-25: Ca^{2+} concentration and $CaCO_3$ precipitation rate as function of NaOH concentration in 50 wt % MEG at 30 ^oC and 1 bar

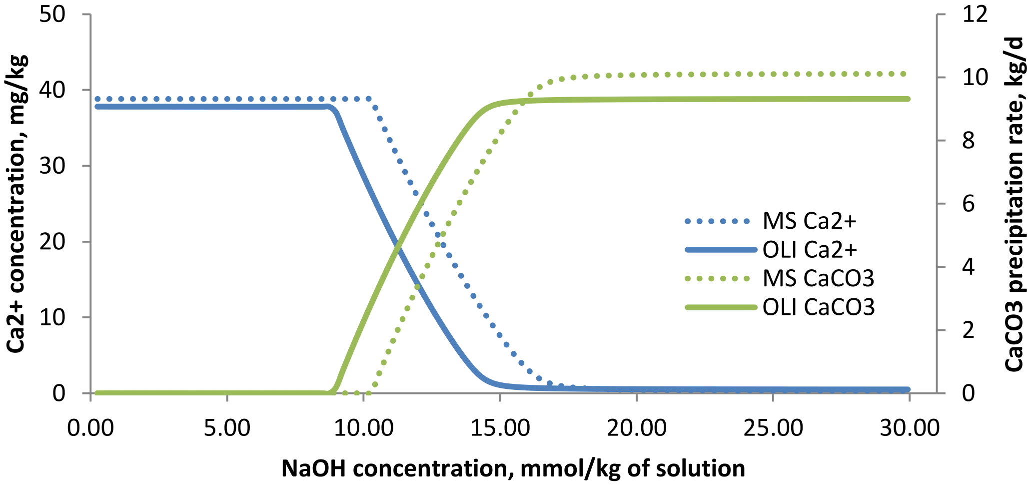

Figure E-26: Ca2+ concentration and CaCO3 precipitation rate as function of NaOH concentration in 50 wt % MEG at 50 ^oC and 1 bar

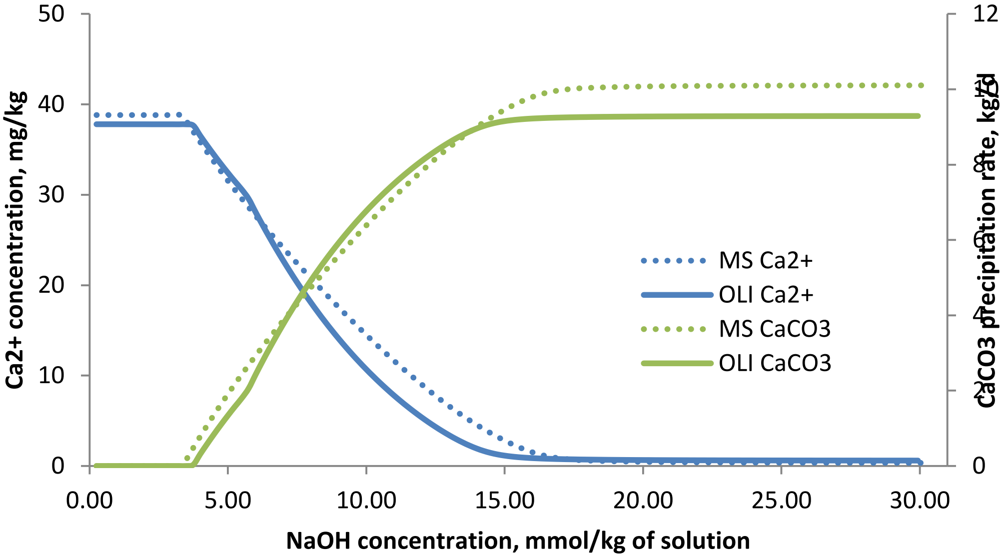

Figure E-27: Ca^{2+} concentration and $CaCO_3$ precipitation rate as function of NaOH concentration in 50 wt % MEG at 80 ^oC and 1 bar

Magnesium Ions

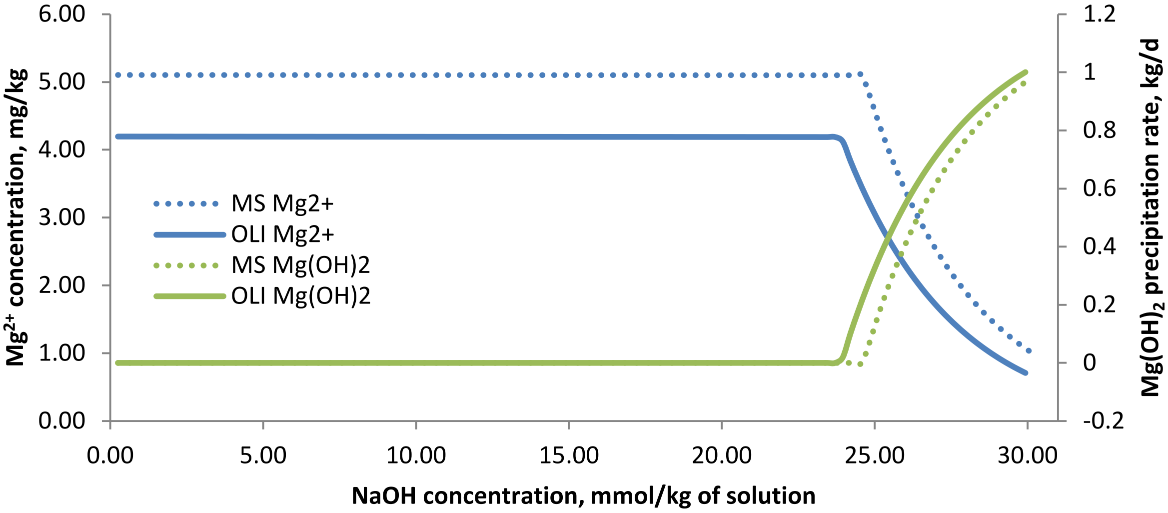

Figure E-28: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of NaOH concentration in water at 70 °C and 1 bar

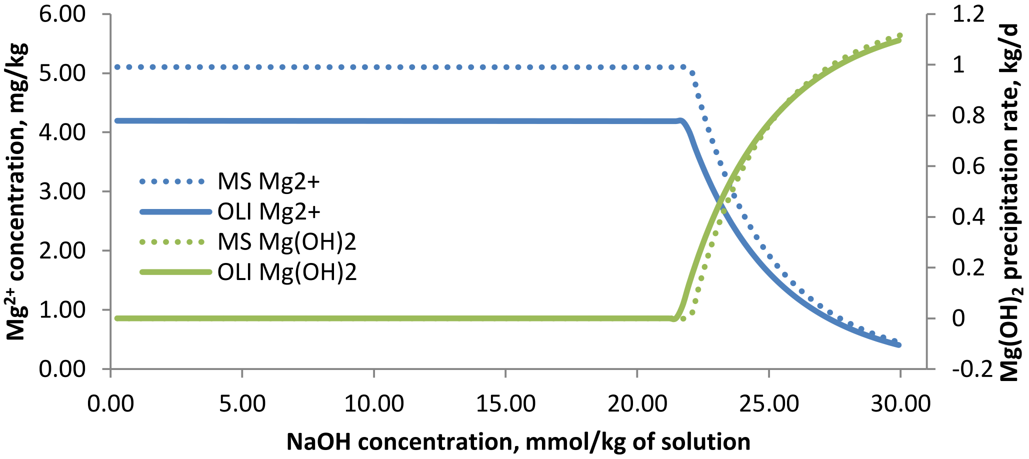

Figure E-29: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of NaOH concentration in water at 80 °C and 1 bar

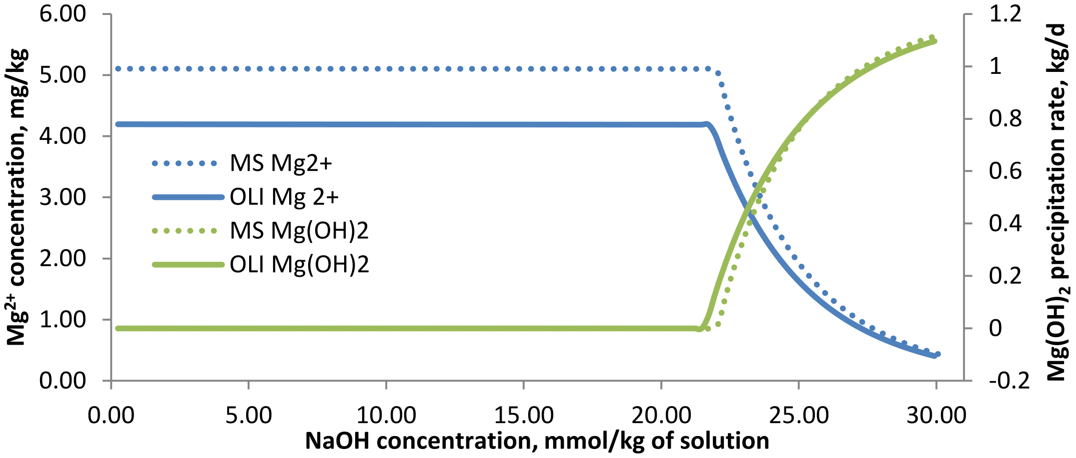

Figure E-30: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of NaOH concentration in water at 90 °C and 1 bar

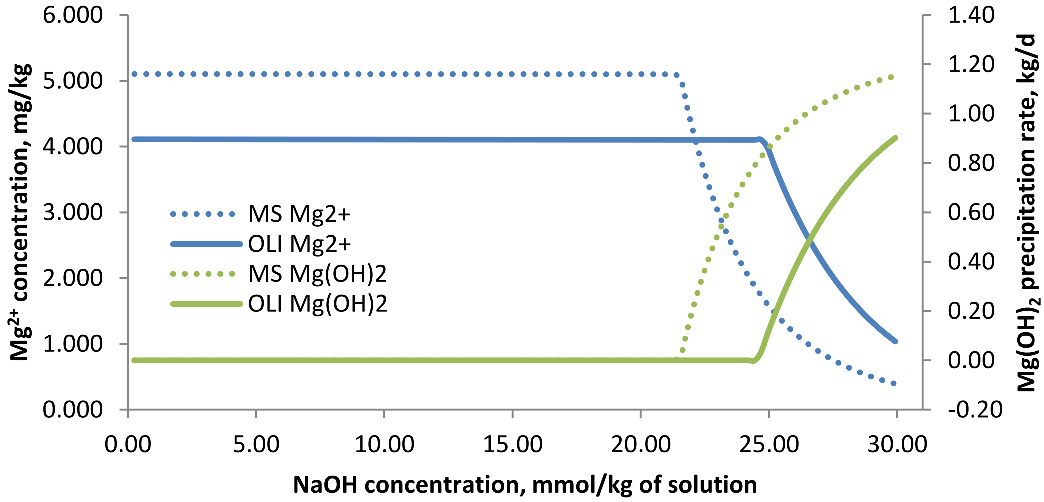

Figure E-31: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of NaOH concentration in 20 wt % MEG at 70 °C and 1 bar

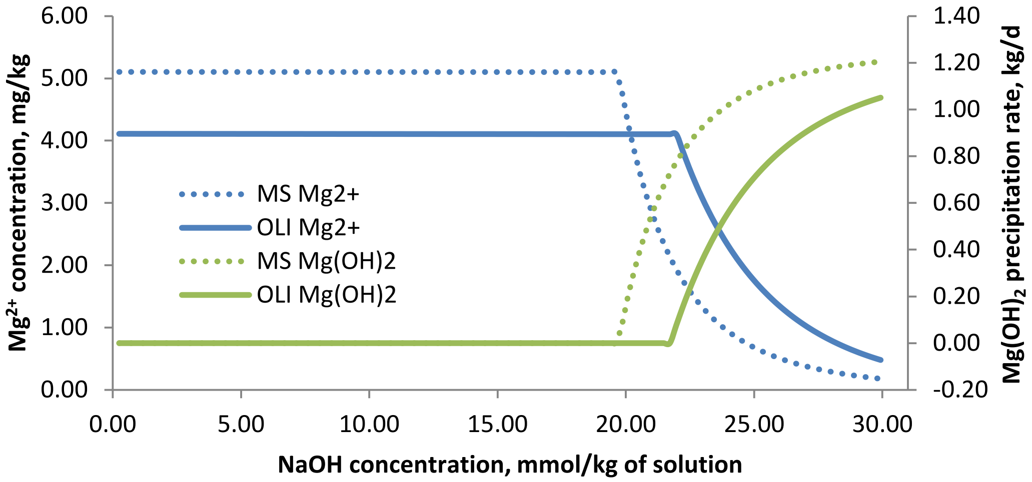

Figure E-32: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of NaOH concentration in 20 wt % MEG at 80 °C and 1 bar

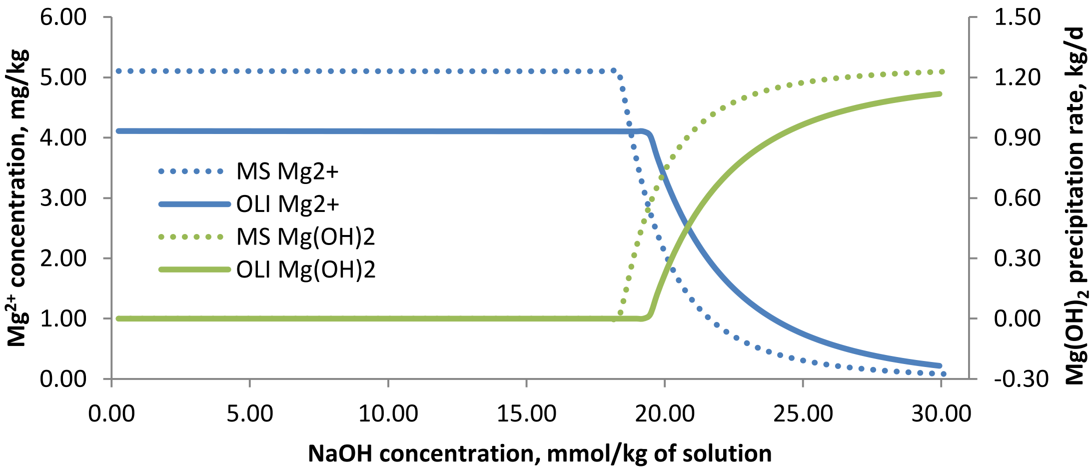

Figure E-33: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of NaOH concentration in 20 wt % MEG at 90 °C and 1 bar

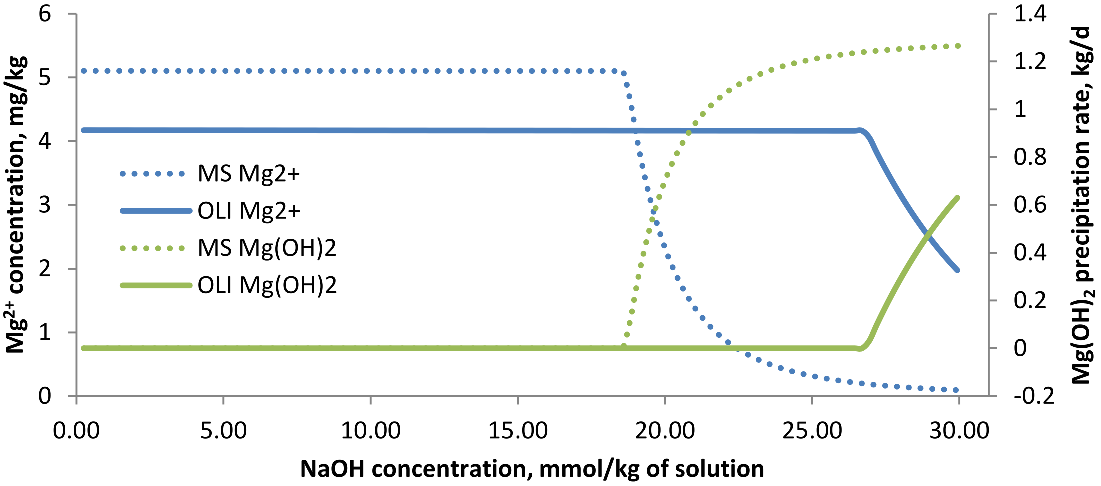

Figure E-34: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of NaOH concentration in 50 wt % MEG at 70 ^oC and 1 bar

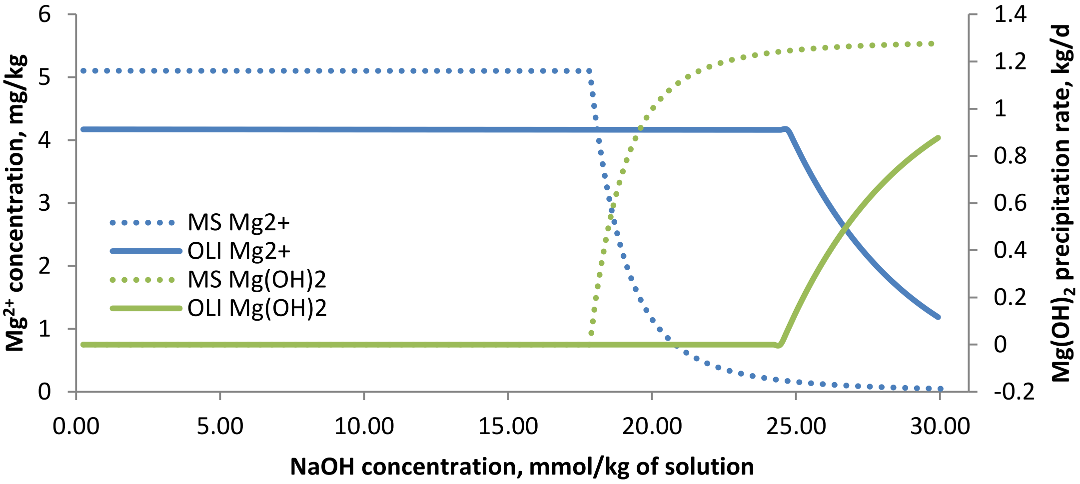

Figure E-35: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of NaOH concentration in 50 wt % MEG at 80 ^oC and 1 bar

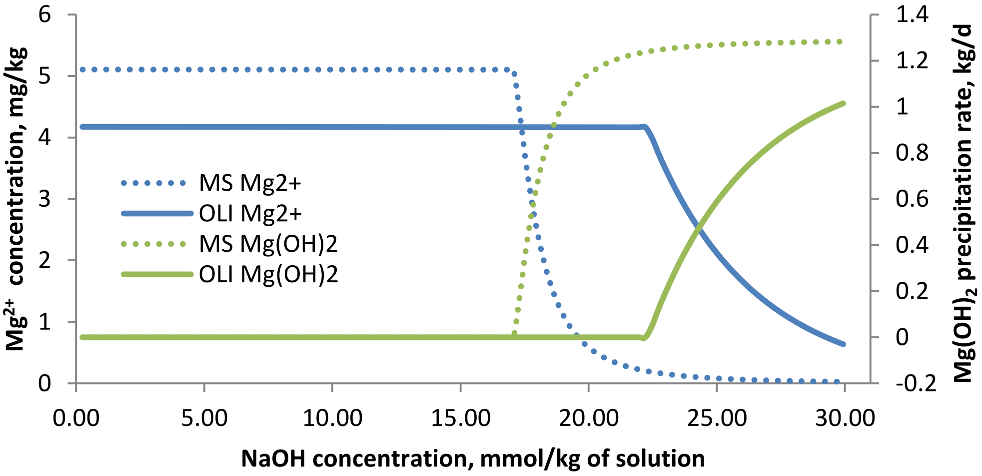

Figure E-36: Mg^{2+} concentration and $Mg(OH)_2$ precipitation rate as function of NaOH concentration in 50 wt % MEG at 90 ^oC and 1 bar