DEVELOPMENT OF A SIMULATOR FOR ETHYLENE GLYCOL LOOPS BASED ON
SOLUTION THERMODYNAMICS AND PARTICLE FORMATION KINETICS

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ABSTRACT

This paper presents and discusses the results of a joint industry project to predict precipitation
of solids in MEG-systems used for long-distance tie-ins of unprocessed gas directly from subsea wells. Better understanding of the kinetics of dissolution and precipitation reactions in the MEGsystem forms
a basis for improved system design and operation.

Keywords: Hydrate inhibition, glycol, solid precipitation, simulation

INTRODUCTION

MEG Loop Functions

Long gas/condensate subsea tie-ins require effective hydrate prevention, corrosion control, and
minimal risk of mineral scaling. Monoethylene glycol (MEG) is the most viable hydrate inhibitor for such
applications. A closed MEG loop is a means to reduce chemical loss and hence environmental impact. Figure 1 shows the outline of a typical MEG loop. The Kjeller MEG Loop project has focused on mineral scale precipitation and controlled salt removal with fields with considerable formation water production in mind.
The challenge in a MEG loop with regard to salt production is to assure flow from the well all through to MEG treatment system and force precipitation in pre-treatment and reclaimer. The points of most concern are: The MEG injection point, the pipeline, the separation system and the salt removal system.

At the injection point where the lean MEG is mixed with the production stream there is risk of precipitation when the MEG contains alkalinity and the produced water is calcium rich. But supersaturation with respect to calcium carbonate may not lead to adverse scaling, as calcium carbonate nucleation and growth are not spontaneous processes. Both take place on a measurable time scale that can be determined.

Water condenses in the pipeline and makes the MEG more water rich. Corrosion products from the steel wall are mixed into the MEG-water phase. At the receiving facilities the rich MEG may have an iron concentration close to or above saturation. The MEG, formation water and condensed water are separated from the gas and condensate at the host facility. The rich MEG is heated and depressurized to remove dissolved hydrocarbons. During this process the aqueous phase may become supersaturated with respect to carbonates, but again it is possible to predict precipitation rates when the nucleation and growth kinetics are known.

The design of the MEG re-concentration system depends on the salt production rate. With high salt production rates, it is necessary to run the whole MEG stream through a reclaimer to remove water and salt. With low salt production rates it is possible to regenerate most of the MEG in a re-boiler or
pre-concentrator to remove water and control the salt content in the lean MEG by running a slip stream through a reclaimer. The latter configuration is difficult to handle if the MEG is alkaline and contains reasonable high calcium and iron levels.

Extensive precipitation and scaling may take place in the re-boiler when MEG is heated and concentrated. The most viable solution is then to remove calcium- and iron carbonate and other sparingly soluble salts in a pre-treatment system. Based on known precipitation kinetics it is possible to design pre-treatment systems that effectively remove magnesium, calcium and iron. The advantage is twofold: Limited precipitation in the reboiler and limited build up of metal dichloride MEG complexes in the reclaimer.

The main salt produced in the reclaimer is sodium chloride. It is seldom a challenge as it usually forms crystals in the 1/10 mm range which settles readily. Carbonates and sulphates are more of a challenge as they form smaller particles that are more difficult to settle as the liquid viscosity increases due to increasing salt concentration. Precipitating carbonate in a reclaimer may also be a challenge as carbonate may decompose to hydroxide and CO₂ with prolonged residence times at high temperature.

THE KJELLER MEG LOOP (KML) SIMULATOR

The Simulator is the “complete” simulation model for a facility. It is complete in the sense that it contains relevant thermodynamic models and models for the removal rate of ionic species due to precipitation. It does not model all the equipment in a facility, but includes major process components and pipelines relevant to control the use and recycling of MEG and the behavior of chemicals carried by the water-MEG mixture. Figure 2 shows a MEG loop simulator with the relevant units.

FIGURE 2 - Example of a MEG Loop simulator
The MEG Loop simulator shall predict phenomena occurring over long time horizons, typically days to months, perhaps years. The purpose is not to resolve detailed dynamic transients, but more long-term precipitation and dissolution of chemicals within the system. Therefore, most of the equipment may be assumed to be in a quasi steady state within each time step, with only slow changes in accumulated masses of key chemicals. However, the calculations in the simulator are dynamic; the chemical state changes within each time step and mass is moved forward to the next block.

The simulation software has a modular structure, where each block in the software, called Unit Models (UMs), can be selected from a model library containing numerous types of such models to be linked to form the total model. The user selects what to include in the simulator by means of a Graphical User Interface (GUI). Normally, a UM is a model of a certain type of equipment, for example a flash tank.

The streams temperature, pressure, fluid composition and flow rate are prescribed at upstream boundaries. These may be varied during a simulation. The user normally specifies temperatures and pressures in process components, except where temperature or pressure calculations are necessary to secure consistency. Flow rates and phase compositions, and chemical concentrations, are calculated dynamically. The simulator is able to follow the build-up of chemical contents due to “chemical sources”, and/or inadequate removal processes, and slow dynamics due to changing reservoir conditions. Mass conservation is observed, and internal volumes in process equipment are accounted for. Where applicable, phase volumes are specified by the user, except in units specifically designed to have a variable holdup.

A process stream describes the flow of fluids from one unit model to another. The stream contains the total flow rate, the relative amounts of aqueous, vapor, hydrocarbon liquid and any solid phases, in addition to temperature and pressure. The compositions of all phases are known.

A unit model in general has a set of user specified parameters, a set of state variables, a set of inlet and outlet connections for process streams, and methods for calculating the outlet streams when the inlet streams are known.

The Thermodynamic Models

In order to find a stable solution of the chemistry of a whole MEG Loop, the simulator cannot rely on sequential solution of the mass balance. This requires the sensitivities of all the mixed equilibrium kinetic problems; i.e. partial derivatives of the free energy with respect to the species involved have to be calculated. The thermodynamic models in the simulator are a Peng-Robinson or Soave-Redlich-Kwong equation-of-state for the gas phase. The aqueous phase modeling comprises Helgeson-Kirkham-Flowers Equation-Of-State for aqueous and the UNIQUAC excess function.

The chemical reactions can either be characterized as at equilibrium or by rate-limiting reactions. For equilibrium reactions, the computations are calculated from a minimizing of the chemical potential. Irreversible chemical reaction rates are calculated by a package that is common to all the unit models in the simulator. The reaction rates are formulated in terms of pressure, temperature, and concentrations.

Model for Rate-Limiting Reactions

Modeling of electrolytic compounds in the aqueous phase is at the heart of the purpose of the simulator. The focus has been on the kinetics of precipitation of carbonates of calcium originating from
the reservoir and iron as a result of corrosion. Detailed experimental results have been reported previously\textsuperscript{11-15}.

To a large degree the nucleation and growth rates of calcium- and iron carbonate determine the de-supersaturation downstream the MEG injection point and in the process system. The growth on a given number of particles will determine the final size of the particles that are to be separated out and might also provide information about the amount of scaling on the surfaces.

The situation is complex for calcium carbonate which has three polymorphs, vaterite, aragonite and calcite, with different nucleation and growth rates as function of temperature and MEG-contents\textsuperscript{16}. All three polymorphs precipitate at MEG-loop conditions, but it has been shown that the vaterite is favored at high MEG-contents whereas aragonite dominates at higher temperatures. However, due to transportation through the MEG-loop the different polymorphs might grow at conditions where they would not form spontaneously. The overall growth rate, i.e. the extension of a linear dimension for the crystals over time, can be given as:

\[ G[m/s] = k_g \left(\sqrt{SR} - 1\right)^g \]

\[ j[\#/m^3s] = k_j \left(\sqrt{SR} - 1\right)^j \]

where SR is the saturation ratio, \( k_g \) is the growth rate constant, and g is the growth order providing information about the actual mechanism of growth. The growth rate constant and order parameter are calculated based on de-supersaturation measurements in seeded batch experiments as a function of MEG-content and temperature for the different polymorphs. Although depending on the level of supersaturation, a growth order parameter value of 2 seemed to describe most situations, showing that crystal growth is limited by the integration at the crystal surface. The growth rate constants in water at 40 °C were found to be 3.2, 0.9, and 0.7 nm/s for vaterite, aragonite, and calcite, respectively. In 50 wt% MEG the growth rate constants were reduced to 19%, 7%, and 44% of the corresponding water-value. An increase in temperature from 40 to 70 °C caused a three-fold increase in the growth rate constant of vaterite.

The nucleation rate follows a higher order dependency with respect to supersaturation but can be expressed by a similar power law expression as the crystal growth rate:

where \( k_j \) is the nucleation rate constant and j is a number found to be in the range of 3-7 for the most relevant MEG-loop conditions. The nucleation rate constant was modeled by measuring the effect of MEG concentration and temperature on crystal numbers and the induction time for numerous unseeded batch experiments\textsuperscript{17}. Table 1 gives the results. Due to the high variance in polymorphic content, the rate constant is a lumped value for the polymorphic mix that would form spontaneously at any point in the MEG-loop.
TABLE 1 – NUCLEATION RATE CONSTANTS AND NUCLEATION ORDER

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Wt% MEG</th>
<th>j</th>
<th>(k_j) [m(^{-3})s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>50</td>
<td>7.0</td>
<td>10(^{1.8})</td>
</tr>
<tr>
<td>40</td>
<td>70</td>
<td>3.8</td>
<td>10(^{3.8})</td>
</tr>
<tr>
<td>70</td>
<td>50</td>
<td>4.8</td>
<td>10(^{4.3})</td>
</tr>
<tr>
<td>70</td>
<td>70</td>
<td>3.8</td>
<td>10(^{4.6})</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The KML simulator comprises all units needed to simulate a MEG Loop.

The kinetics of salt precipitation of carbonates of calcium originating from the reservoir has been studied in unseeded and seeded batch experiments to investigate the nucleation rate and growth rate in different solvent compositions and temperatures, representative for typical locations within the MEG-loop. The nucleation and growth rates were modeled as power-law relationships as a function of the activity-based supersaturation ratio with a rate constant that varies for the different polymorphs increasing with temperature and decreasing with the MEG-content.

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REFERENCES


