

EUTECTIC FREEZE CRYSTALLIZATION (EFC): A COOL SOLUTION FOR PROCESSING GEOTHERMAL WASTE BRINES?

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ABSTRACT

To minimize fossil fuel combustion, geothermal heat production is increasingly applied in the horticultural sector and for domestic heating in The Netherlands. One of the major operational challenges for further development of geothermal energy in The Netherlands is dealing with the large volumes of geothermal brine that are produced during well development. In contrast with discharging the brine as an environmental waste or highly energy-demanding evaporative methods, eutectic freeze crystallization (EFC) could be both be a sustainable and cost-effective method. Applying EFC on a multicomponent solution as a geothermal brine results in a lower freezing point and eutectic temperature. With EFC the aim is to separate saline water into re-usable products: pure water as ice and pure salts that precipitate at their eutectic crystallization points, requiring relatively little energy compared to evaporative methods. In this study we performed a first technical and economical evaluation of the potential of EFC in treating geothermal brine using EFC lab experiments on synthetic brines and hydrogeochemical modelling of known geothermal brines. Results show significant technical and economic potential in producing pure water (as ice) during freeze concentration and subsequently Hydrohalite ($\text{NaCl}\cdot 2\text{H}_2\text{O}$) precipitation hydrohalite (at $\sim 21^\circ\text{C}$) from the geothermal brines during EFC from geothermal brines in The Netherlands. Due to the dominance of sodium and chloride in the considered Dutch geothermal brines, the results from the developed PHREEQC model for the simulation of EFC on geothermal brines indicate that it is not economically attractive to produce the other salts, as the precipitate out at much lower ($< -40^\circ\text{C}$) degrees and only in minor amounts.. To maximize the usability of the ice and salt produced during EFC of geothermal brines, future studies should assess how to operationally maximize the purity of the ice and salt produced and the extent to which (in)organic traces are incorporated. The largest potential for brine concentration using freeze concentration was for the relatively low salinity brine of the carboniferous limestone and Delft sandstone formations. The

geothermal brine from the Slochteren formation provides the highest potential for hydrohalite production. The production of products (ice, salt) of high enough purity to allow re-use requires further study on actual geothermal brines with more complex brine composition than considered in this study. However, freeze concentration is already a commercially available method for brine treatment, and should be considered as an option for the concentration of geothermal waste brines. Overall, freeze concentration can result in significant reduction of the waste stream and the potential to produce usable water while using eutectic salt precipitation may produce significant yields of hydrohalite with economic value.

1. INTRODUCTION

To minimize fossil fuel combustion, geothermal heat production is increasingly applied in the horticultural sector and for domestic heating in The Netherlands. One of the major operational challenges for further development of geothermal energy in The Netherlands is dealing with the large volumes (3500-6000 m³ per well) of geothermal brine, also called testwater, that are produced during well development (Bakema et al. 2016; Hartog 2016). This highly saline test water, geothermal brine, is currently temporarily stored in foil basins until processing (Figure 1).



Figure 1: Example of a basin containing geothermal brine (testwater) produced during the development of a geothermal system in The Netherlands (Hartog, 2016).

Since re-injection of the waste brine has so far been associated with significant risks for clogging and/or damaging the newly developed wells, finding

environmentally and financially acceptable options has been challenging. For example, legal permission to discharge to sewer, or by pipeline to sea or river has been increasingly difficult to obtain. Also, the alternative of transport of the waste brine by truck ($\sim 30\text{m}^3$) to a specialized waste treatment facility has been both financially and operationally unattractive. In a recent evaluation (Bakema et al. 2016), various standard techniques for on-site waste water treatment, including on-site evaporation and reverse osmosis, have been considered either unpractical for highly saline conditions, too costly, or both.

An approach that has not been considered thus far for the treatment of geothermal waste brine is the use of freezing methods, such as freezing concentration or the relatively new eutectic freeze crystallization (EFC). These methods rely on freezing rather than evaporation to concentrate the brine. Since the freezing of water requires six times less energy than evaporation (Lewis et al. 2010), freeze concentration could provide an energy-efficient alternative. In addition, during EFC ice and subsequently salt(s) are formed separately (Figure 2) which generates waste-to-product potential.

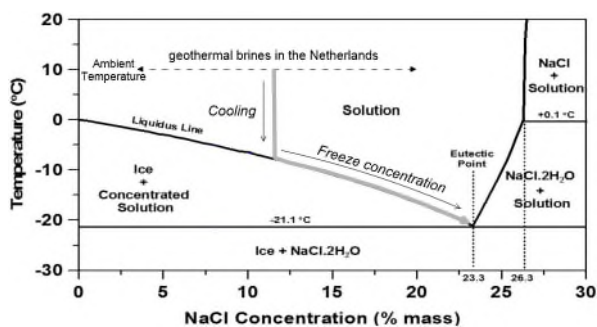


Figure 2: Phase diagram for the binary Na-Cl/H₂O system, with the range of geothermal brine salinities in the Netherlands at average ambient temperature. The salinity of the composite brine (Table 1) is used to illustrate the cooling and subsequent freeze concentration stage towards the eutectic point.

Eutectic Freeze Crystallization (EFC)

During eutectic freeze crystallization (EFC) a saline solution is first cooled until ice is formed at its freezing point (grey line in Figure 2). As the ice is formed, the salinity of the remaining solution increases (freeze concentration) and further cooling is required for additional ice formation. This will continue until the eutectic point is reached, where the solution also becomes saturated for the (first) salt. All the ice formed at this point will therefore also result in the precipitation of the salt. For solutions with an initial concentration above the eutectic point, first salt precipitates upon cooling and then ice starts forming after reaching the eutectic point is reached upon further cooling.

Ideally, separation of the solid ice and salt formed separates out, as driven by gravity, due to the large

density difference between the concentrated brine and the precipitated salt (sinks) and the formed ice (floats).

GOAL OF THIS STUDY

In this study it was aimed to perform a first evaluation of the potential of EFC as an option for processing geothermal waste brine produced in the Netherlands. To this end, theoretical, experiment and modeling analyses were performed, lab experiments were conducted and a EFC PHREEQC model was developed to conduct hydrogeochemical modelling of EFC on geothermal brine compositions.

2. METHODS

2.1 EFC experiments

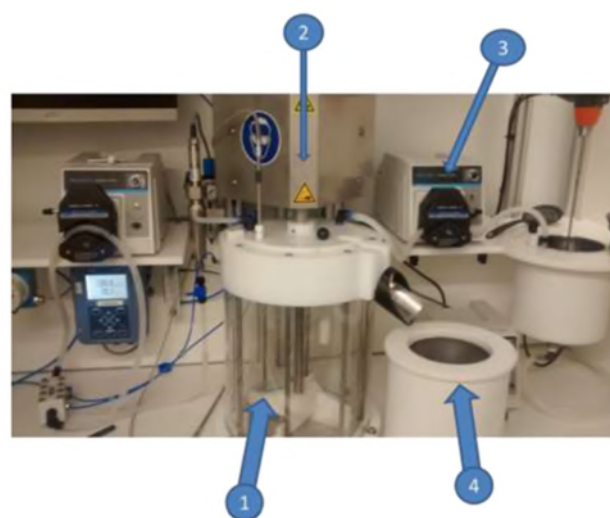


Figure 3: Set-up of EFC experiments including a reactor vessel (1) with an agitator, and a cooler at the bottom of the vessel that is driven by a motor (2). Furthermore; a sample pump (3) and a collection vessel (4) in which a solid/liquid filter and a vacuum pump were placed.

To test the operational conditions for EFC application on geothermal waste brines, EFC experiments were carried out in the KWR laboratory on several synthetic solutions. The experimental EFC set-up consists of a reactor vessel in which an agitator and a cooler ("crystallizer") are placed (Figure 3). The agitator was used to ensure a well-mixed solution during the experiments. Solution samples were taken by the peristaltic sample pump and salt and ice are separated by a solid/liquid filter and a vacuum pump, which is placed in the collection vessel. In the experiments EFC was applied to a 21 wt.% NaCl solution and on a "composite brine" with concentrations within the range of geothermal brine conditions in the Netherlands (Table 1, Figure 4). Each experiment started with cooling the cooling fluid for one night to $-15\text{ }^\circ\text{C}$. Then,

using a cooling fluid ($\sim -35^\circ\text{C}$) in the cooler surrounding the reactor to provide cooling power, the solution was further cooled down to (first) eutectic temperature (eutectic point). In order to increase the purity of the ice produced during the experiments, the ice was washed (two times) with deionized water of 5°C .

Table 1: Initial composition of the “composite brine”, representing a geothermal brine composition, and its composition after the EFC experiment. The calculated freeze concentration factor (FCF) is indicated for the cations.

Element	Initial (mg/L)	After EFC (mg/L)	FCF
Na^+	66600	64050	0,96
Cl^-	82156		
Mg^{2+}	265	720	2,72
Ca^{2+}	2525	7555	2,99
K^+	215	560	2,6

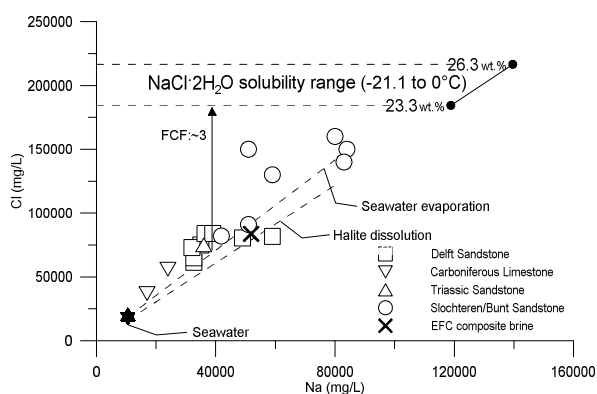


Figure 4: Sodium (Na) versus chloride (Cl) concentrations in geothermal brines from the Netherlands clustered based on their reservoir formation. Also the composite brine composition used in the experiments and modelling is shown. FCF: Freeze concentration factor.

2.2 Hydrogeochemical Modelling

To evaluate the development of ice formation and salt precipitation for multi-component brine compositions, the program PHREEQC (version 3.4.0) was used to develop a model of the EFC process applied on geothermal brines of different composition. Since EFC operates at temperatures below 0°C and geothermal brines are of relatively high ionic strengths, a database obtained by Toner and Catling (2017) was used for which ice was defined as a separate phase. This Pitzer database is valid from 25°C to $< -73^\circ\text{C}$. The database contains data for only the Na-K-Ca-Mg-Cl-SO₄ system. The initial temperature of the geothermal brine was set at 15°C , an approximation of the temperature after the brine has cooled during storage at ground surface. The temperature was then decreased stepwise to 0 and then -63°C . The charge balance was

maintained on chloride as it is the dominant anion throughout the EFC process. At temperatures below -40°C numerical errors in maintaining the charge balance due to the limited amount of solution remaining. For temperatures below -63°C PHREEQC could not compute the concentrations of the elements in solution, as these became too low for all simulations. All minerals present in the Toner & Catling database were set to have a target saturation index of 0.

3. RESULTS AND DISCUSSION

3.1 EFC experiments

During the EFC experiment for the 21 wt.% NaCl solution, the cooling power was raised after 9,5 hours, resulting in a short period of further cooling, until ice formation started at a temperature of about -16°C (Figure 5). The slower temperature decrease while cooling power remained constant represents the impact of the positive enthalpy change resulting from the phase change of water to ice. Then, after 12.5 hrs at a temperature of -21°C , also hydrohalite started forming, its crystallization enthalpy resulting in further decrease in the temperature decline rate.

The EFC experiment for the composite brine resulted in a similar temperature development (not shown) with only a slightly lower temperature for the eutectic point at -22°C by the presence of the additional salt components (Table 1). The concentrations of Mg, Ca and K showed similar 3-fold increases in concentrations in solution after the EFC experiment. As none of these elements seem to have undergone precipitation, this indicates that two-third of the initial water had been converted to ice. Contrary to what was expected, the Na concentration was similar to initial and had not increased to concentration expected when reaching the eutectic point (~ 185000 mg/L, Figure 4, Figure 5), but had remained 3-fold lower. Also, there had only been visual observation of ice formation at the top of the reaction vessel, not of NaCl precipitation at the bottom. Therefore, it seems that all NaCl precipitated that stuck to the ice formed, suggesting that the NaCl crystal sizes formed were too small to sink to the bottom of the reactor under the force of gravity and/or hampered by the use of the agitator.

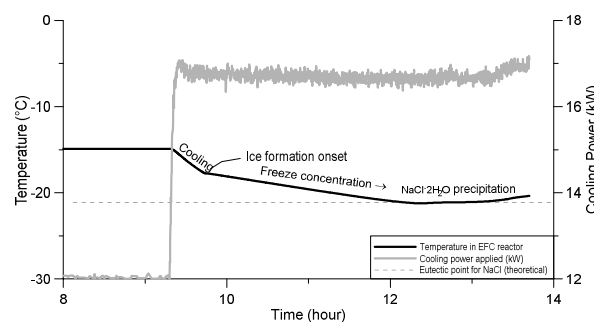


Figure 5: Development of the solution temperature and cooling power applied during the EFC experiment on a 21 wt% NaCl solution. The temperature for the eutectic point for NaCl is shown with the dashed line.

Although the ice and salt could not be separated with this experiment, previous experiments showed that two washing cycles could effectively improve the purity of the collected ice formed. For ice formed from the 21 wt.% NaCl solution, the NaCl concentration in the ice decreased to 1,5–4 g/L after one to two washing cycles, illustrating that the salt crystals were present mainly at the residual brine at the surface of the ice mass.

3.2 Hydrogeochemical EFC modelling

The application of the EFC PHREEQC model for the “composite brine” (Table 1) indicated that ice formation started at -13.6°C and hydrohalite (Figure 2) precipitation at -21.4 °C (Figure 6), slightly warmer than was observed during the experiment (22°C). The total amount of ice formed at the eutectic point of hydrohalite is between 30 and 60% of the original water volume (Figure 6), in keeping with the 3 fold increase in concentration of remaining salts in the final brine composition of the composite brine experiment (Table 1). The conservative enrichment Mg, K and Ca at the eutectic point during the experiment. The model results indicates that the other chloride salts do start to precipitate in the model until temperature drops below -40°C (Figure 7).

Modelling EFC on a simplified composition of the relatively saline geothermal brine from the Slochteren/Bunt formation, showed that a minor amount (0.0015 kg) of gypsum already precipitated at the onset of the simulation. At a temperature of -19 °C, ice started to crystallize (Figure 8), a lower freezing point than for the less saline composite brine. The majority of the ice is formed before and at the eutectic temperature of hydrohalite (NaCl·2H₂O) at -23 °C, only slightly colder than for the composite brine. The calculated highest yield of this salt was about 0.3 kg. Only at temperatures below -37 °C the salts sylvite (KCl), MgCl₂·12H₂O and antarcticite (CaCl₂·6H₂O) precipitated (Figure 8) in minor yields of about 0.004, 0.03 and 0.1 kg respectively. These minerals are also known to precipitate in nature at these low temperatures (Bakker and Baumgartner 2012).

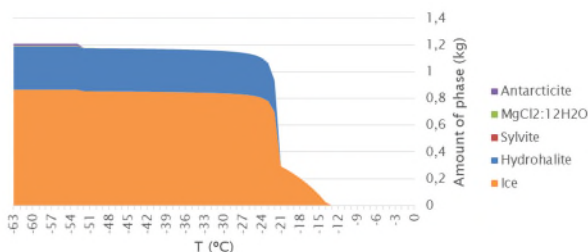


Figure 6: The amount of salts and ice formed during EFC on the composite geothermal brine (Table 1) as calculated by the EFC PHREEQC model. The initial amount of water was 1 kg.

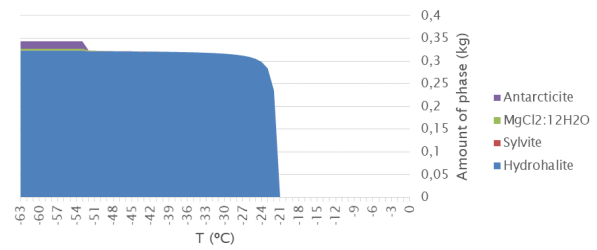


Figure 7: The amount of salts formed during EFC on the composite geothermal brine (Table 1) as calculated by the EFC PHREEQC model. The initial amount of water was 1 kg.

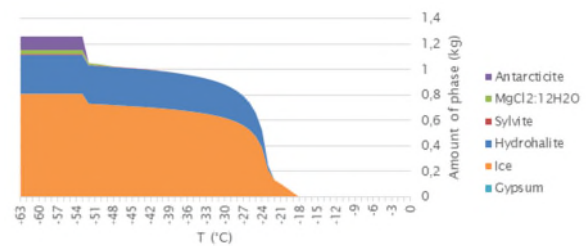


Figure 8: The amount of salts and ice formed during EFC on a geothermal brine composition from the Slochteren/Bunt formation (Figure 4) as calculated by the EFC PHREEQC model. The initial amount of water was 1 kg

The model results for the geothermal brines from Delft Sandstone formation (Figure 9) showed a relatively high freezing point of -7°C, in line with their relatively low salinity (Figure 4).

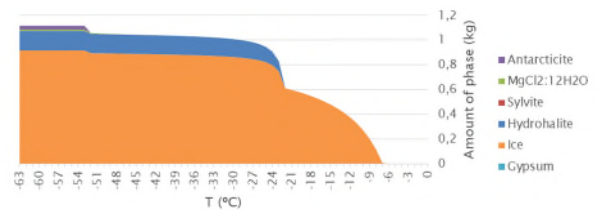


Figure 9: The amount of salts formed during EFC on a geothermal brine composition from the Delft Sandstone formation (Table 1) as calculated by the EFC PHREEQC model. The initial amount of water was 1 kg.

Overall, for the range of geothermal brine compositions in the Netherlands, all PHREEQC simulations indicated that hydrohalite precipitates much sooner than other chloride salts and produces the highest salt yield, ranging from 50 to 80% of the total salt yield. In a few cases minor amounts of gypsum precipitates before freezing occurs or co-precipitates at a similar eutectic temperature as for hydrohalite.

3.3 Practical applicability of freeze concentration and EFC

The results of this study show that a relatively large fraction of ice can be formed during freeze concentration before hydrohalite starts to precipitate, ranging from 10% per kg initial water for the most saline Slochteren brine (Figure 8) to 60% for the less saline brines from the Delft Sandstone formation (Figure 9). This results in freeze concentration factors of 30% brine volume reduction for the most saline Slochteren brines to 600% for the least saline brines from the carboniferous limestone reservoirs. Combined with the precipitation of hydrohalite during at its eutectic temperature, the use of EFC holds promise of producing usable products. While freeze concentration is a water treatment technology already on the market, producing re-usable products with EFC is still in the development stage. Earlier studies have concluded however that EFC is technically feasible at larger scales (Nathoo, Jivanji, and Lewis 2009; Lewis et al. 2010; Randall, Nathoo, and Lewis 2011; Jivanji 2011; De Graaff 2012; Manana, Nembudani, and Rodriguez-Pascual 2015; Adeniyi et al. 2016). Therefore, developing a mobile full scale installation should have priority to enable EFC the production of usable products from geothermal brines. While for the geothermal brines from the saline Slochteren formation highest economic potential would come from the use of EFC for the production of halite, the use of freeze concentration above the eutectic temperature of hydrohalite could already be an attractive option for waste brine reduction and water production.

With the observed residual salt concentrations in the ice produced during EFC of only a few gram per litre, the salinity can be reduced 25-100 fold from initial brine concentrations. Although this facilitates discharge, further treatment would be required to allow use, e.g. as drinking or irrigation water.

3.4 Perspective on future research

The results of this study clearly indicate that sodium and chloride are the main constituents to consider in the evaluation of EFC potential on geothermal brines in the Netherlands with hydrohalite as the most important potential salt yield. However, further research should focus on ways to increase the purity of the produced ice further, e.g. through the use of ice seeding. Also, the complexity of geothermal brine chemistry should be considered in more detail than is currently possible with the low temperature database of Toner and Catling (2017) that only covers the Na-K-Ca-Mg-Cl-SO₄ system. Not only are more phases expected to precipitate, also ensuring the purity of the precipitated phases will be more challenging. In addition to extending the database to include more species, EFC experiments should be conducted on actual geothermal brines that focus on the compositional development of the solution and the purity of the phases formed. Also, the research should focus on the composition of the brine after it has been produced and cooled at earth surface already leads compositional changes, e.g. the

gypsum precipitation as shown in our modelling results or the carbonate precipitation resulting from CO₂-degassing (Hartog 2015), and should thus be considered to make the study of EFC application more realistic.

4. CONCLUSIONS

In this study the potential of freezing methods for the treatment of geothermal waste brine in the Netherlands was investigated. Based on the first analysis, modelling and experiments in this study, the use of freezing methods for the treatment of geothermal waste brines seems promising. Freeze concentration can result in significant reduction of the waste stream and the potential to produce usable water while using eutectic salt precipitation may produce significant yields of hydrohalite with economic value. As shown by the experiments, hydrohalite is the main salt to be produced (at ~-21°C) from the geothermal brines, as the other chloride salts precipitate out at much lower (<-40°C) degrees and only in minor amounts.

As illustrated with the EFC experiment with the composite brine, the presence additional chloride salt constituents did only slightly reduce the eutectic temperature, therefore the energy required for hydrohalite production seems insensitive for the range of geothermal brine compositions in the Netherlands. Using the EFC PHREEQC model showed that within this range for geothermal brines the largest potential for brine concentration using freeze concentration was for the relatively low salinity brine of the carboniferous limestone and Delft sandstone formations. The geothermal brine from the Slochteren formation provides the highest potential for hydrohalite production. The production of products (ice, salt) of high enough purity to allow re-use requires further study on actual geothermal brines with more complex brine composition than considered in this study. However, freeze concentration is already a commercially available method for brine treatment, and should be considered as an option for the concentration of geothermal waste brines.

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