Modeling systems containing fluoride in addition to H_2O – (K^+, Na^+, H^+, Ca^{2+}) – (Cl^-, HSO_4^-, SO_4^{2-}, OH^-, CO_2, HCO_3^-, CO_3^{2-}, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-})

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Introduction

In the first part of this project, a thermodynamic model for the description of the phase relations in systems containing the main components H_2O, − (K^+, Na^+, H^+, Ca^{2+}) − (Cl^-, HSO_4^-, SO_4^{2-}, OH^-, CO_2, HCO_3^-, CO_3^{2-}, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) was developed. In this second report, it is described how the modeling was extended to also include the fluoride ion. Other components, that will later be added, are aluminum ions, iron(iii) ions, copper ions, and cadmium ions.

Model parameters for the above system have not previously been published in the open literature. A model for the subsystem consisting of the sodium, fluoride, and phosphate ions was published by Weber *et al.*[1] in 2000. That model was targeted on the problem of treating radioactive wastes, where otherwise uncontrolled precipitation would occur. All the experimental data that were used for determining parameters in the model by Weber *et al.* were also used in the current work. In addition, the thermodynamic modeling in this report is also based on experimental data involving potassium, calcium, chloride, sulfate, and carbonate ions.

Experimental data were found in IVC-SEP's data bank for electrolyte solutions. This data bank was available for the project due to Kommunekemi's membership of the IVC-SEP consortium.

Experimental data were measured at temperatures from the freezing point of the solutions and up to 200 °C. Most of the data are valid at temperatures below the normal boiling points of the solutions. The model is therefore valid in the temperature range from the freezing point of the solutions and up to 100 - 120 °C.

Thermodynamic model

The thermodynamic model applied in this work is the Extended UNIQUAC model. The model has previously been described in the litterature [2, 3, 4]. The model is an activity coefficient model and contains the following three terms:

1. A Debye-Hückel term for describing electrostatic interactions between ions in the solution.
2. A UNIQUAC term, to describe the interactions between ions and water, in addition to non--electrostatic interactions between ions.
3. A Soave-Redlich-Kwong term, describing the deviation from ideality of the gas phase. This last term is only important when a gas phase is in equilibrium with the electrolyte solution at relatively high temperature.

The performance of the Extended UNIQUAC model, which was developed at DTU Chemical Engineering, has recently been compared with the performance of two of the most well known

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[1] CF Weber, EC Beahm, DD. Lee, and JS. Watson, "A Solubility Model for Aqueous Solutions Containing Sodium, Fluoride, and Phosphate Ions", Ind. Eng. Chem. Res., 39(2000)518-526

[2] K. Thomsen P. Rasmussen, and R. Gani, Correlation and prediction of thermal properties and phase behaviour for a class of electrolyte systems, J. Chem. Eng. Science, 51(1996)3675-83

[3] K. Thomsen and P. Rasmussen, Modeling of Vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems, Chemical Engineering Science, 54(1999)1787-1802

[4] K. Thomsen, Modeling Electrolyte Solutions with the extended universal quasichemical (UNIQUAC) model, Pure and Applied Chemistry, 77(2005)531-542

models for salt solutions[5]. These two models are the OLI MSE model from OLI systems (www.olisystems.com) and the eNRTL model from AspenTech (www.aspentech.com). It was concluded in that work that the Extended UNIQUAC model and the OLI model both could reproduce the phase relations in the test solutions with a satisfactory accuracy while the eNRTL model was less accurate. It was the Extended UNIQUAC model with "old" parameters that was compared. It is expected that the new parameters determined in this work would do even better in comparison.

Binary Systems Containing Fluoride

The Sodium Fluoride – Water System

The solubility of sodium fluoride, NaF in water is about 4 mass % at temperatures below 100°C. This is a relatively low solubility and therefore the salt does not reduce the freezing point of water considerably. According to the experimental data, the eutectic point of the NaF-H_2O system is between -3.5 and -2.98 °C. The salt does not form any hydrates, but always crystallizes as NaF. The phase diagram of the NaF-H_2O system is shown in Figure 1. The calculated solubility of NaF is marked with a line and is plotted along with experimental values of the solubility. From Figure 1 it is seen that the experimental data for this system are quite scattered.
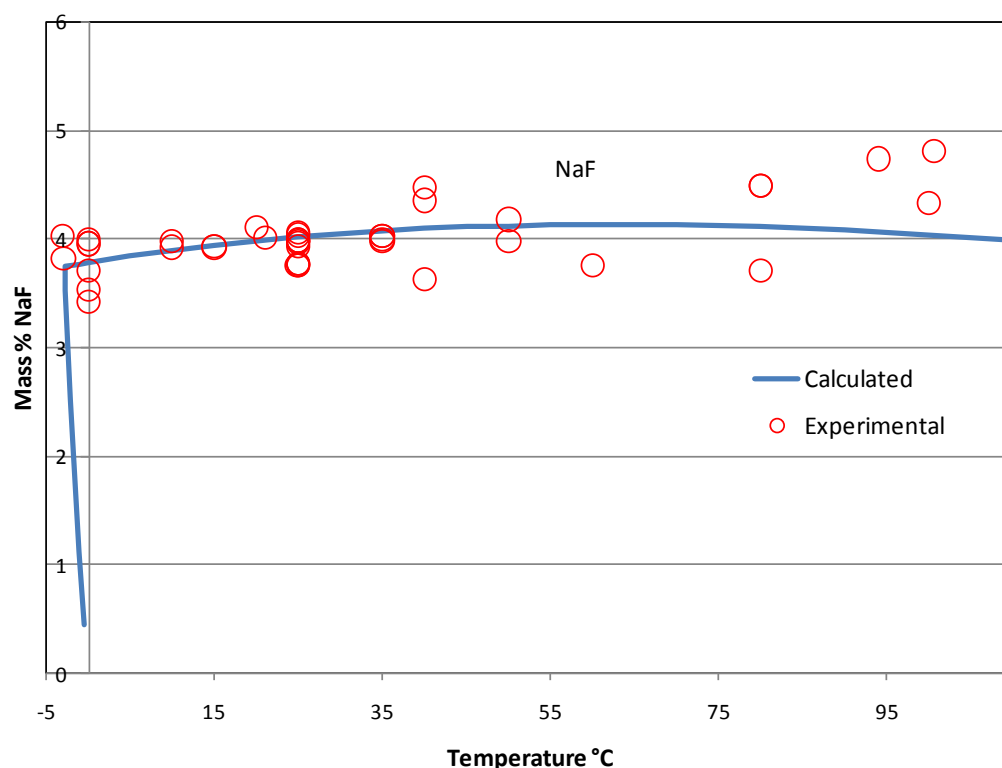

Figure 1: Phase diagram for the binary NaF-H_2O system. The solubility of NaF in water as a function of temperature. Experimental data are shown with circles and the calculated value of the solubility is marked with a line.

[5] Y. Lin, A. ten Kate, M. Mooijer, J. Delgado, PL Fosbøl, K Thomsen, Comparison of activity coefficient models for electrolyte systems. Submitted for publication in AIChE Journal.

The Potassium Fluoride – water system

The solubility of potassium fluoride, KF has strong temperature dependence. The salt is much more soluble than sodium fluoride and it forms two hydrates. The tetrahydrate, $KF \cdot 4H_2O$ is the stable form in equilibrium with a binary solution at temperatures below 17.7 °C. Between 17.7 and approximately 45 °C, the dihydrate, $KF \cdot 2H_2O$ is the stable form. Above 45 °C, the anhydrous form of KF will precipitate from supersaturated solutions. The eutectic point of $KF-H_2O$ solutions is between -21.8 °C and -21.5 °C due to the high solubility of KF. The phase diagram for the $KF-H_2O$ system is shown in Figure 2.
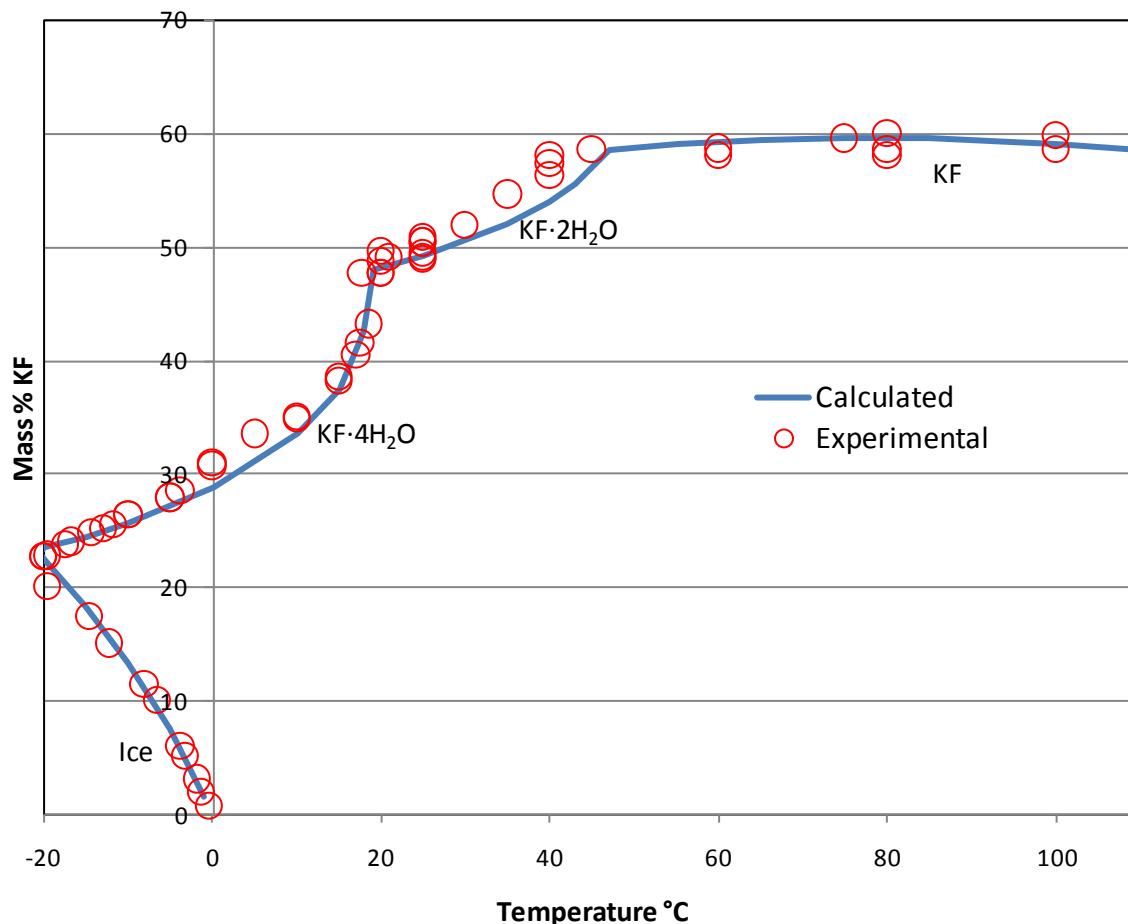

Figure 2: Phase diagram for the binary $KF-H_2O$ system. The solubility of KF in water as a function of temperature. Experimental data are shown with circles and the calculated value of the solubility is marked with a line.

The Calcium Fluoride – Water System

The solubility of calcium fluoride in water is very low and there are only a few experimental determinations of this solubility in the open literature. The four experimental data are not even consistent and it looks like the values at 18 °C are outliers.

As there are no experimental data available at temperatures above 25 °C, the calculated solubility of CaF_2 represents prediction at temperatures above this temperature. According to the available experimental data, CaF_2 does not form any hydrates but always precipitates in the anhydrous form. The phase diagram for the $CaF_2 – H_2O$ system is shown in Figure 3.

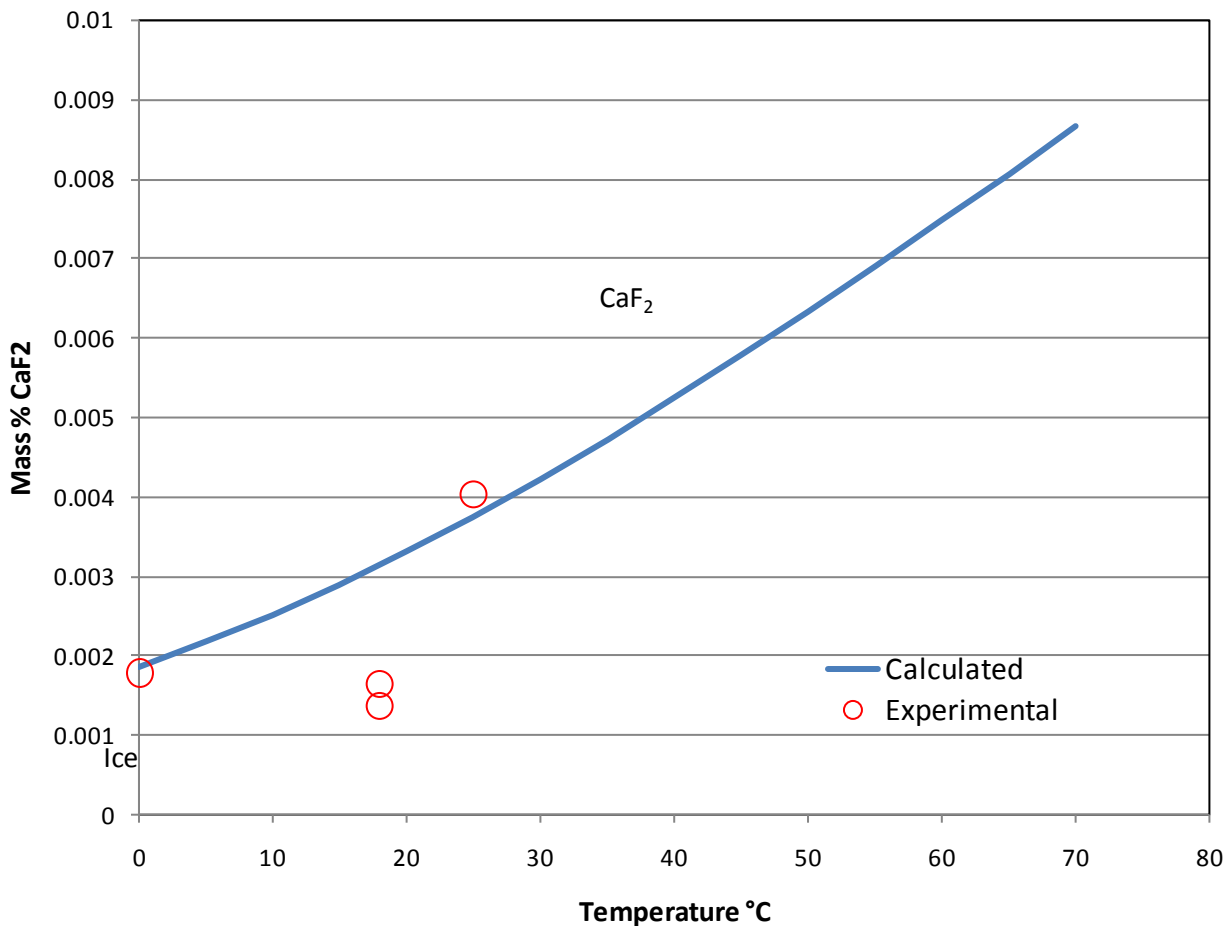Figure 3: Phase diagram for the binary CaF$_2$-H$_2$O system. The solubility of CaF$_2$ in water as a function of temperature. Experimental data are shown with circles and the calculated value of the solubility is marked with a line.

Ternary Systems Containing Fluoride

The Sodium Fluoride – Hydrogen Fluoride – Water System

When a small amount of hydrogen fluoride, HF is added to an aqueous solution of NaF, the solubility of NaF is initially increased. This is a salting in effect. If larger amounts of HF are added, the double salt NaF·HF becomes stable and the solubility drops significantly. This is indicated in Figure 4 which shows how the solubility of NaF is influenced by the addition of HF in concentrations up to 16 mass % at 20 °C. At higher concentrations, the solubility of NaF·HF tends to increase again and salts like NaF·2HF, NaF·3HF, and NaF·4HF become stable.
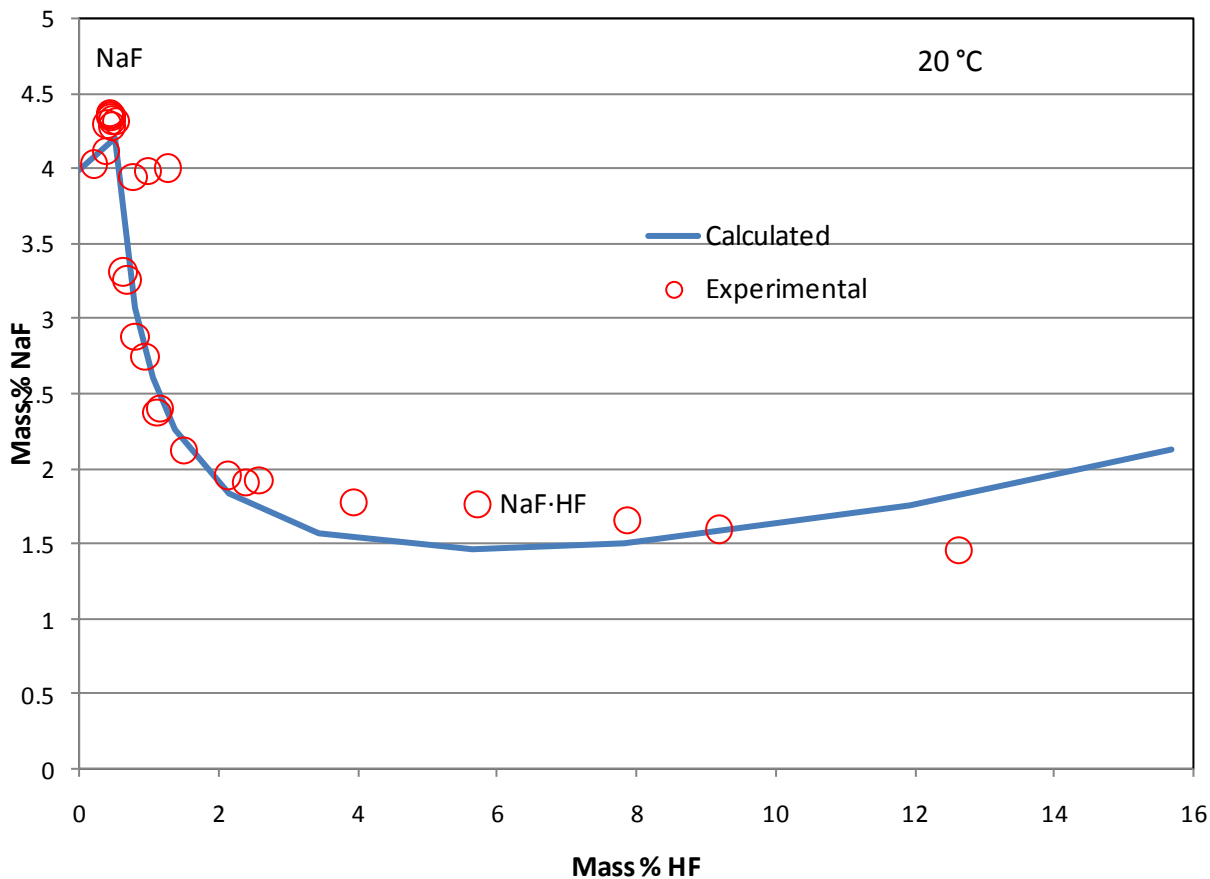
Figure 4: The effect of added HF on the solubility of NaF in water at 20 °C. A small amount of HF gives a salting in effect, which increases the solubility of NaF. At more than 0.5 mass % HF, NaF·HF becomes the stable phase and the solubility decreases sharply. At high concentrations of HF the solubility of NaF·HF increases again.

The Potassium Fluoride – Hydrogen Fluoride – Water System

The phase behavior of the KF – HF - H_2O system is similar to that of the NaF – HF – H2O system with the exception that the solubility is much larger. As an example, the phase diagram is shown in Figure 5 for the KF – HF - H_2O system at 0 °C. Again there is salting in at low concentrations of HF. By adding more HF, the double salt KF·HF becomes stable and the solubility drops. It is not shown in the figure, but at higher concentrations of HF, the solubility of KF·HF increases again. Double salts like KF·2½HF, KF·3HF, and KF·4HF become stable at higher concentrations of HF. The formation of these double salts were not modeled in this work, as they are not relevant to the low concentrations of fluoride found in the ash considered in this project.
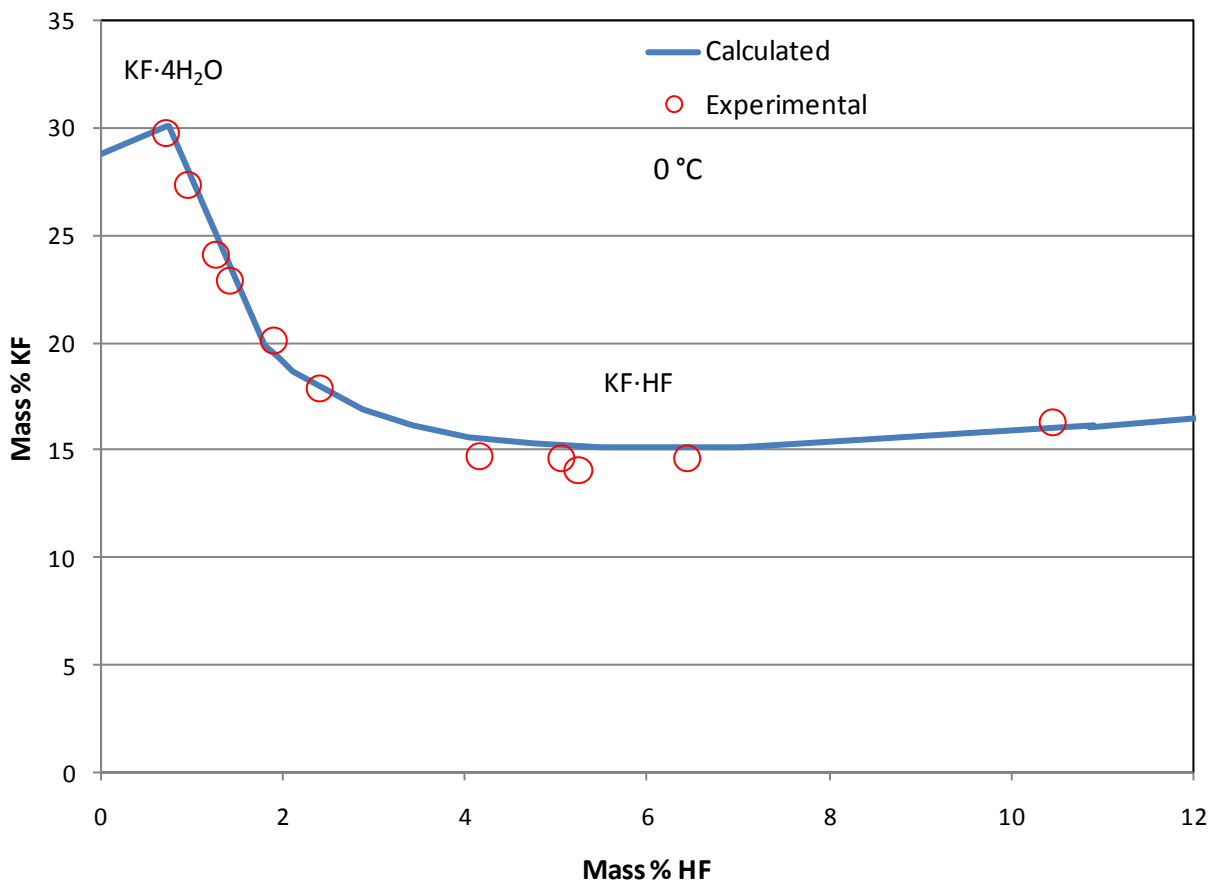
Figure 5: The effect of added HF on the solubility of KF in water at 0 °C. A small amount of HF gives a salting in effect, which increases the solubility of KF. At more than 0.75 mass % HF, KF·HF becomes the stable phase and the solubility decreases sharply. At high concentrations of HF the solubility of KF·HF increases again.

The Sodium Fluoride – Sodium phosphate – Water System

The NaF – Na_3PO_4 – H_2O system is very important in order to determine how phosphate is influenced by the presence of fluoride and vice versa. Two double salts are forming in this system: $2Na_3PO_4 \cdot NaF \cdot 19H_2O$ which apparently form at all temperatures and $2Na_3PO_4 \cdot 3NaF \cdot 18H_2O$ which only appear in the experimental data at 100 °C.

It appears that the experimental data for this system have not been determined with great accuracy. Significant disagreements between experimental data are observed and it is difficult to determine which behavior corresponds to the actual behavior of these solutions. The disagreement is illustrated in Figure 6 and Figure 7. The two phase diagrams concern the temperatures 20 and 25°C. It is obvious that 5 degrees difference should not change the phase behavior as seriously as the experimental data indicate. The experimental data shown in Figure 6 were measured by Guiot[6], who also measured at 0, 40, 60, 80, and 100°C. His experimental work is the only large work that has been performed on this system. Unfortunately the data seem tocontain some systematic error. Weber *et al.*[1] suggest that the measurements by Guiot did not represent equilibrium values as he used a densitometric method of measurement and he apparently did not wait long enough for the attainment of equilibrium.

No experimental data were found for the corresponding KF – K_3PO_4 – H_2O system.

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[6] Guiot J-C., "Etudes sur la système H_2O, Na^+, F^-, PO_4^{---}", Rev. Chim. Minér., 4(1967)85-128
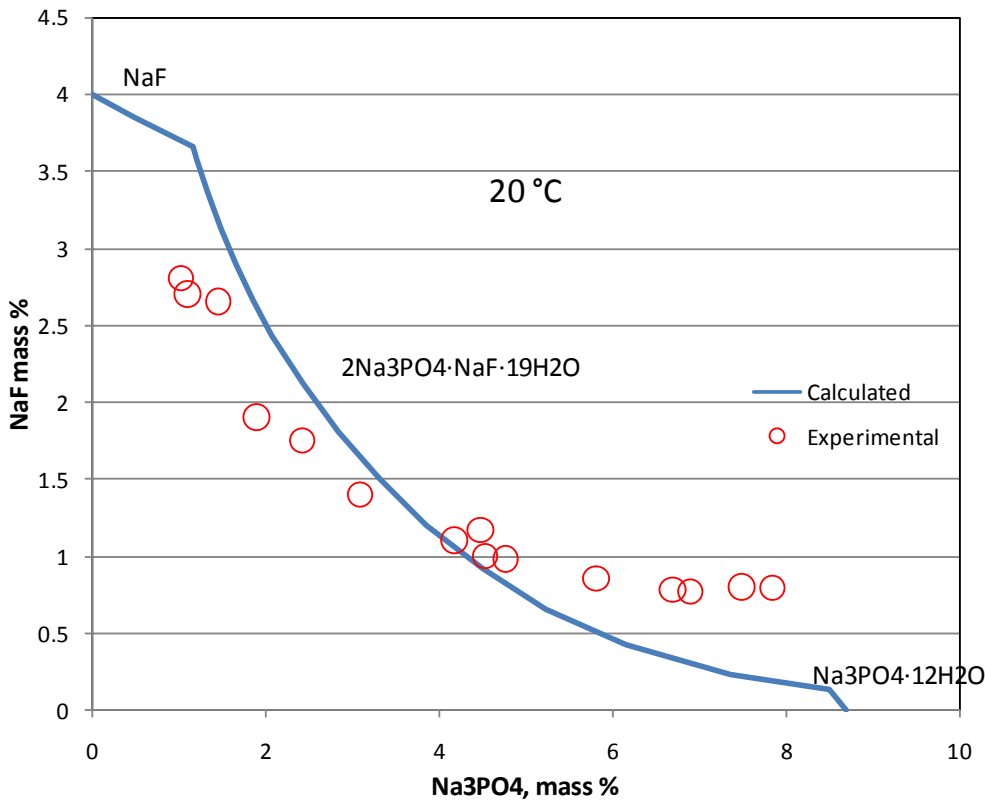
Figure 6: Phasediagram for the NaF − Na₃PO₄ − H₂O system at 20 °C. A large salting out effect is observed in this system. NaF is salted out by Na₃PO₄ and Na₃PO₄ is salted out by NaF and a double salt is formed. The experimental data are marked with circles. It is clear that the experimental data in this figure, valid at 20 °C are not in agreement with the data in Figure 7 which are supposed to be valid at 25°C.
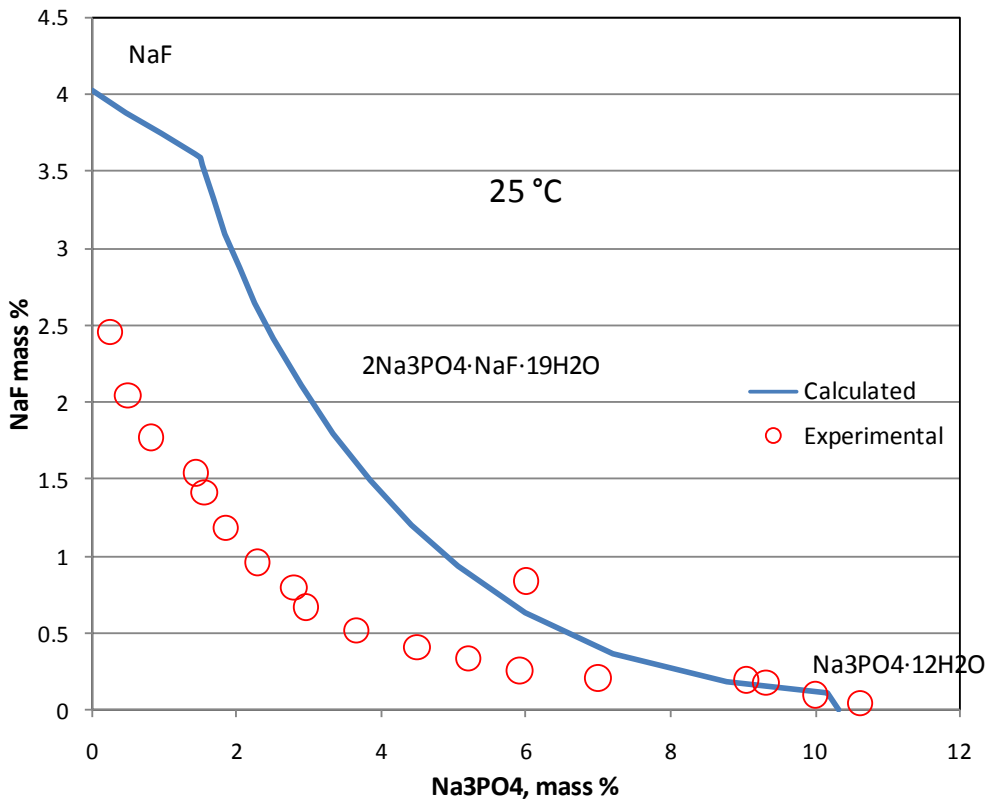

Figure 7: Phasediagram for the NaF − Na₃PO₄ − H₂O system at 25 °C. The experimental data are marked with circles. It is clear that the experimental data in this figure, valid at 25 °C are not in agreement with the data in Figure 6 which are supposed to be valid at 20 °C.

The Sodium Fluoride – Sodium Chloride – Water System

In the NaF – NaCl – H_2O system a strong salting out effect is observed. The solubility of NaF is reduced significantly by the addition of NaCl. This is shown in the phase diagram in Figure 8. In this system there is generally good agreement between calculated and experimental data. No double salts are formed.
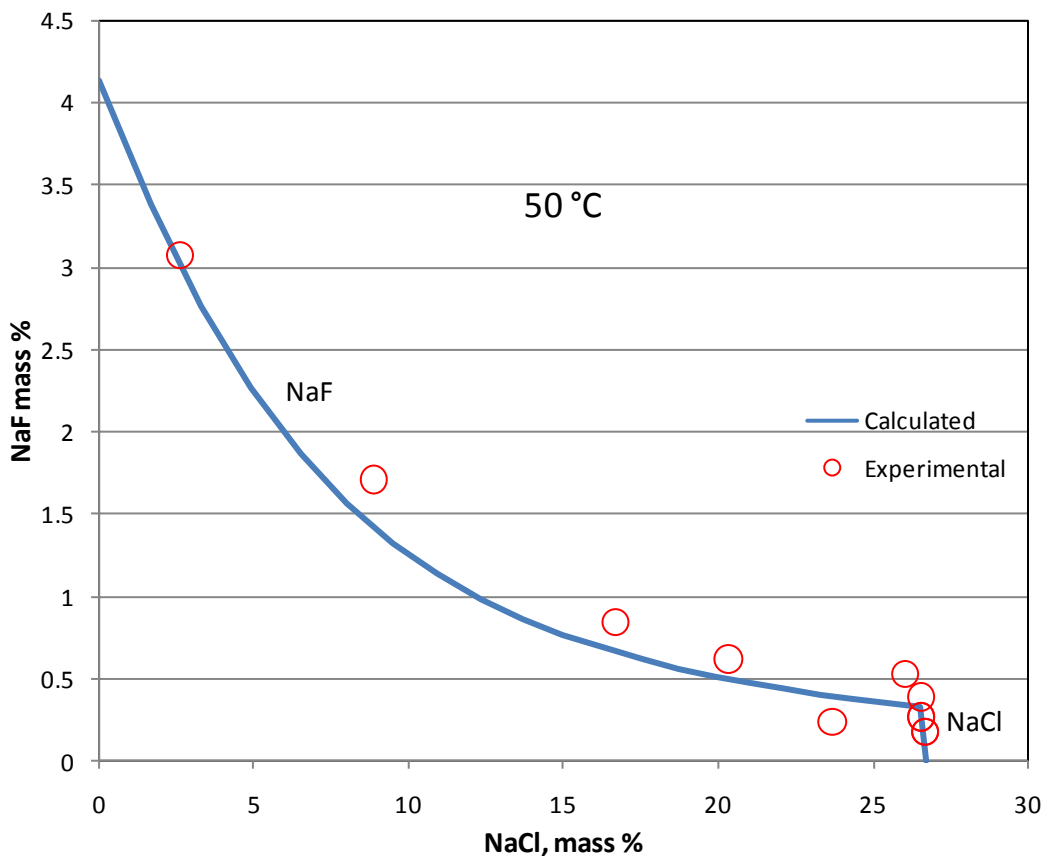

Figure 8: Phase diagram for the NaF – NaCl – H_2O system at 50 °C. Experimental data are marked with circles and the line mark calculated solubility.

The Potassium Fluoride – Potassium Chloride – Water System

Also in the KF – KCl – H2O system a strong salting out effect is observed. But here it is KCl being salted out by the addition of KF. The solubility of KF is only influenced slightly by the addition of KCl. The phase diagram for this system at 25 °C is shown in Figure 9. Experimental data for this ternary system were available at 25 and at 75 °C. At both temperatures, a satisfactory agreement between experimental and calculated data was achieved.
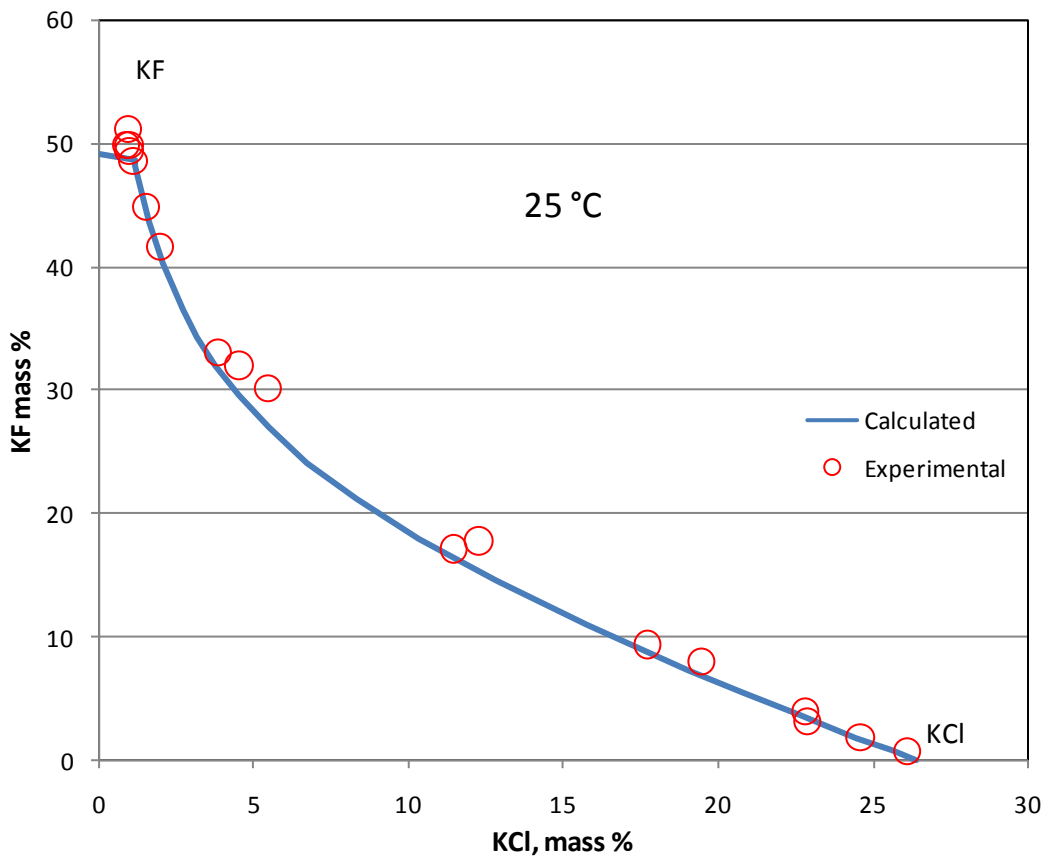
Figure 9: Phase diagram for the KF – KCl – H2O system at 25 °C. Experimental values are marked with circles, while the line marks calculated values.

The Sodium Fluoride – Sodium Sulfate – Water System

A double salt is forming in the $NaF - Na_2SO_4 - H_2O$ system. $NaF \cdot Na_2SO_4$ can precipitate from solutions at temperatures above 17.5 °C. The phase diagram for this system at 35 °C is shown in Figure 10. Experimental data for this system are available at many temperatures between -3 and 50 °C. A good agreement between experimental and calculated data is generally achieved at all temperatures for this system.
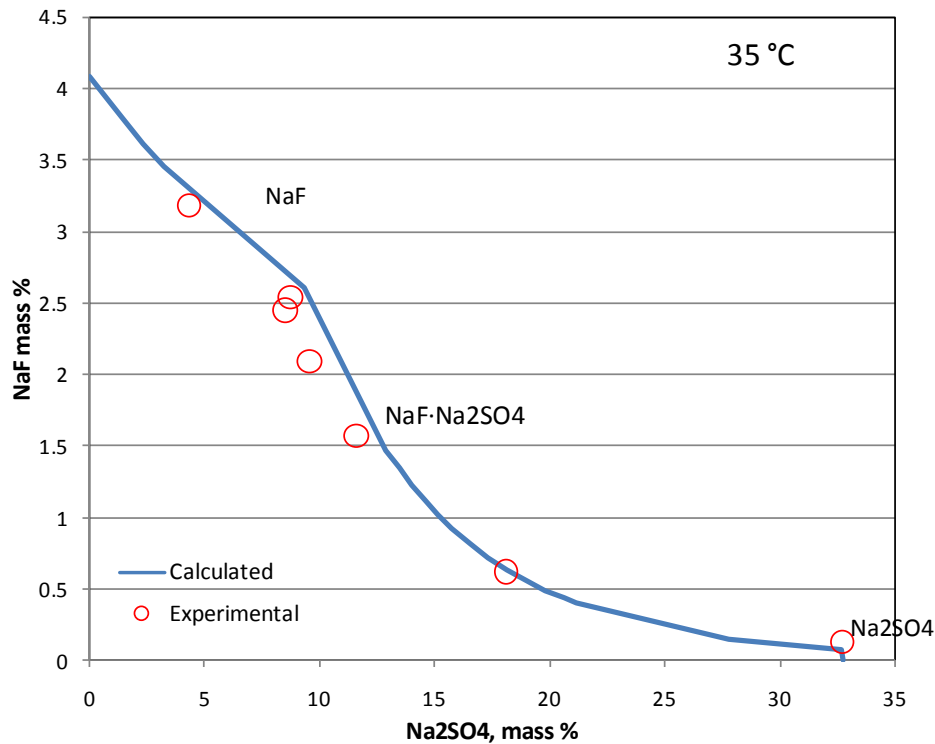
Figure 10: Phase diagram for the NaF – Na2SO4 – H2O system at 35 °C

The Sodium Fluoride – Sodium Hydroxide – Water system

NaF is being salted out by the addition of NaOH. A phase diagram for this ternary system at 20 °C is shown in Figure 11.
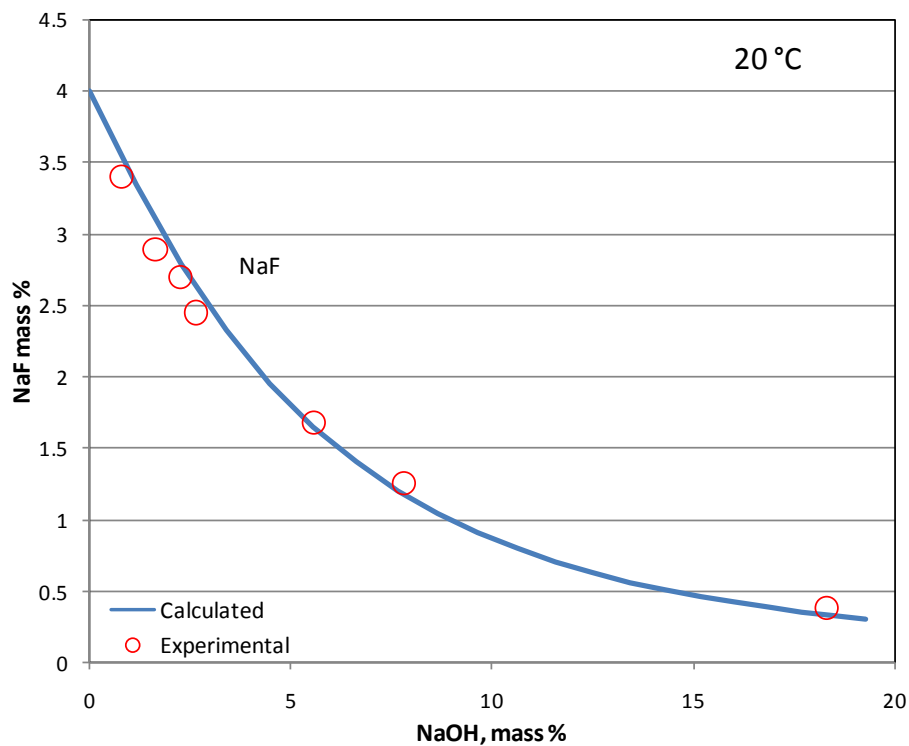

Figure 11: The solubility of NaF as a function of the amount of NaOH added at 20 °C

Also KF is salted out by the addition of KOH. KF is much more soluble than NaF, so contrary to NaF, KF remains quite soluble even by the addition of 20 or 30 mass % KOH. The phase diagram of the KF – KOH – H_2O system is shown in Figure 12.
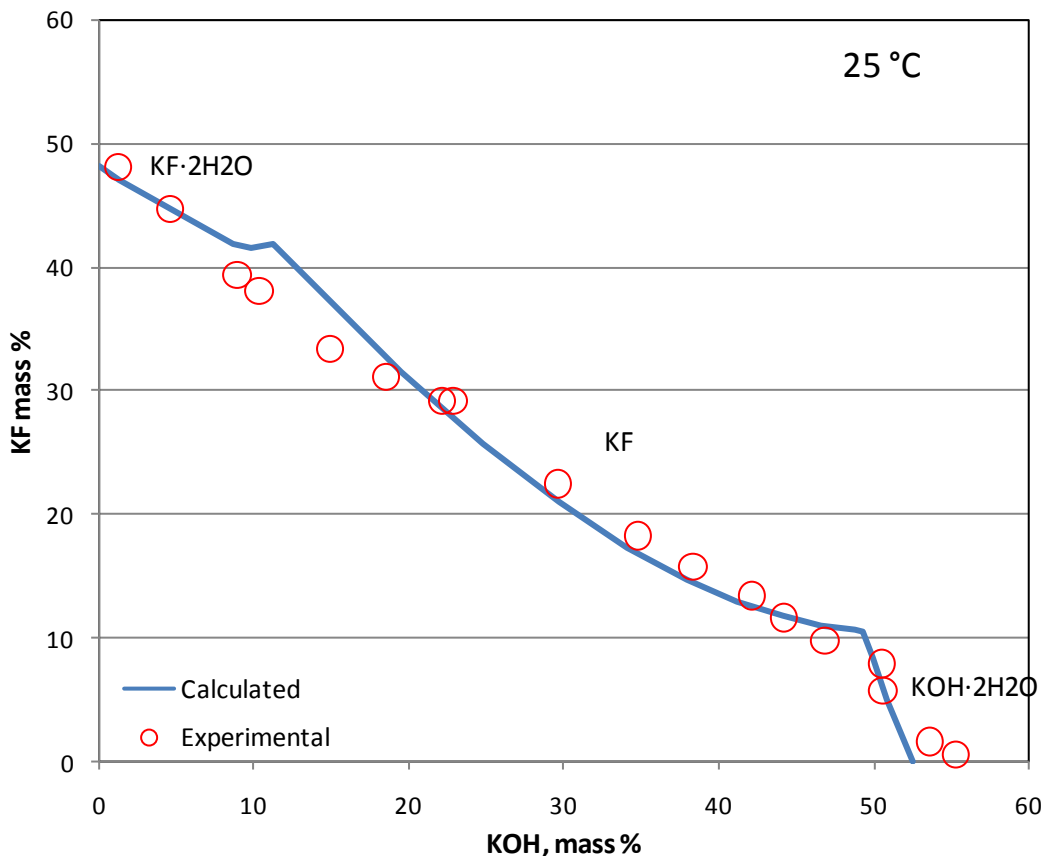

Figure 12: The solubility of KF when KOH is added in different amounts at 25 °C.

The Sodium Fluoride – Sodium Carbonate – Water System

Data for three isotherms, 0, 25, and 50 °C were available for this ternary system. The calculated 50 °C solubility isotherm is shown in Figure 13 along with experimental values. Also in the NaF – Na_2CO_3 – H_2O system, NaF is salted out by the addition of Na_2CO_3. No experimental data for the corresponding potassium system were available.
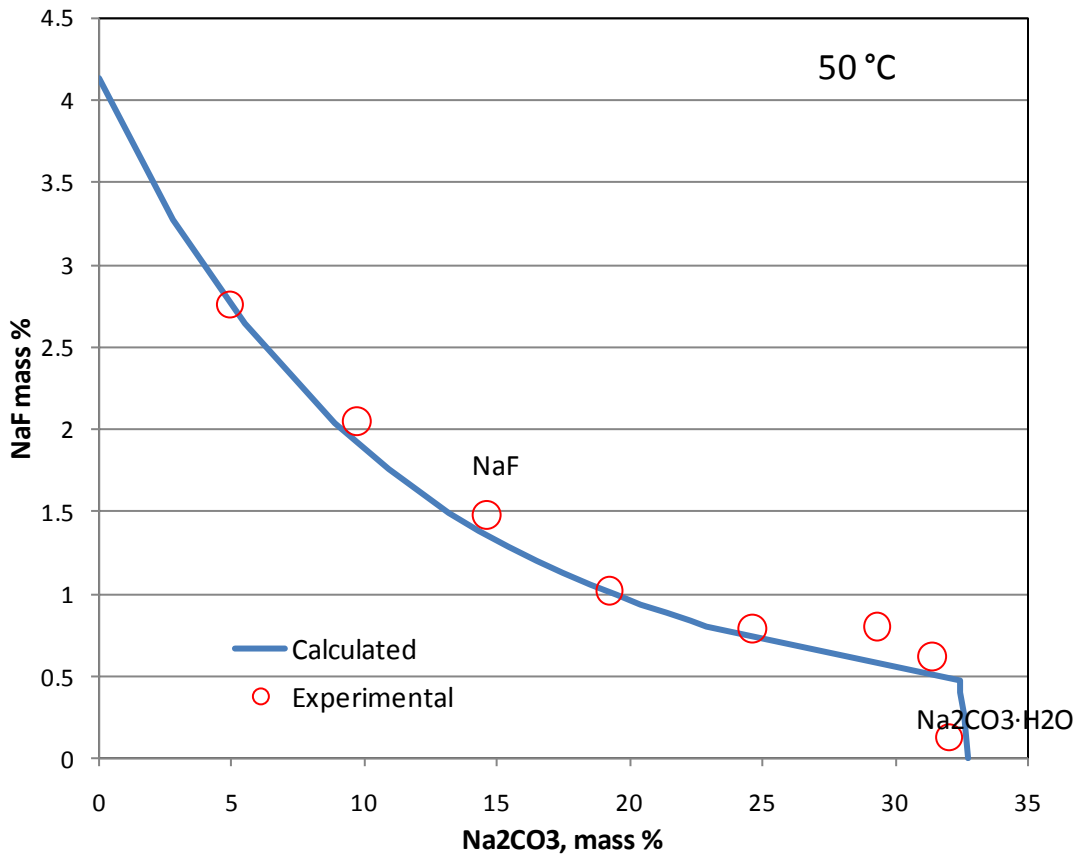
Figure 13: Phase diagram for the NaF – Na$_2$CO$_3$ – H$_2$O system at 50 °C

The Sodium Fluoride – Sodium Bicarbonate – Water System

Only data in a 0 °C isotherm are available for the NaF – NaHCO$_3$ – H$_2$O system. This isotherm is shown in Figure 14.
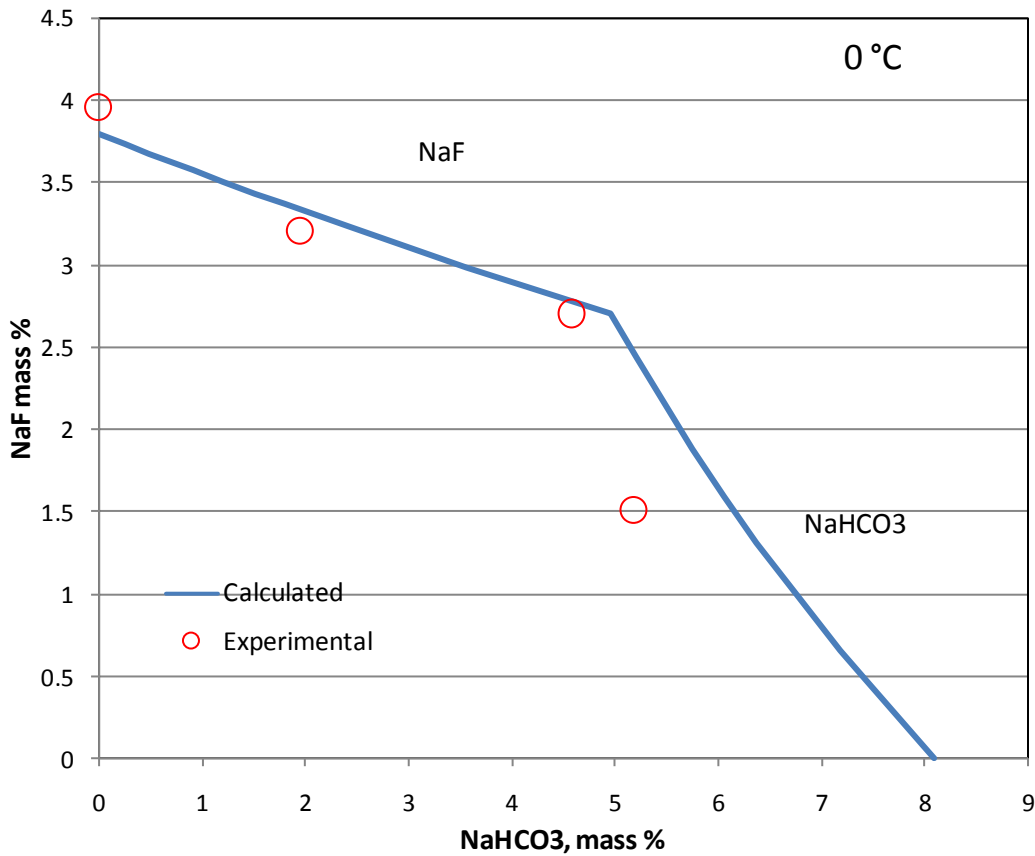
Figure 14: 0 °C isotherm for the NaF – NaHCO$_3$ – H$_2$O system.

Conclusion

In this part of the project, model parameters for the fluoride ion were determined so that phase equilibria in solutions containing fluoride in addition to H$_2$O, – (K$^+$, Na$^+$, H$^+$, Ca^{2+}) – (Cl$^-$, HSO$_4^-$, SO$_4^{2-}$, OH$^-$, CO$_2$, HCO$_3^-$, CO$_3^{2-}$, H$_3$PO$_4$, H$_2$PO$_4^-$, HPO$_4^{2-}$, PO$_4^{3-}$) can be determined.

In general, a good agreement between calculated and experimental data could be obtained. In the case of the NaF – Na$_3$PO$_4$ – H$_2$O system, there were large disagreements between the data from different sources. It is not clear which of these data are most correct – if any. If additional data are found in the literature, the F – PO$_4$ interaction parameter in the model can probably be determined with greater accuracy and a new version of the program IVCKKEM8.DLL be made available.