Modeling systems containing aluminum in addition to H_2O – (K^+, Na^+, H^+, Ca^{2+}) – (F^-, 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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Aqueous Solutions Aps
CVR nummer 31 28 02 30

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Introduction

In the first and second parts of this project, a thermodynamic model for the description of phase relations in systems containing the main components H_2O, – (K^+, Na^+, H^+, Ca^{2+}) – (F^-, 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 third report, it is described how the modeling was extended to include aluminum species. Iron(iii) ions, and copper ions will later be added to the model.

Model parameters for the above system have not previously been published in the open literature. The modeling presented in this report can therefore not be compared to previous modeling projects.

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 valid at temperatures from the freezing point of the solutions and up to 200 °C were used for determining parameters in the model. Most of the applied data are only 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.

The thermodynamic model used for the modeling is the Extended UNIQUAC model. The model was described in the first two reports of this project.

Chemistry of aluminum systems

Aluminum ions in solutions hydrolyze according to the equilibrium:
$$Al^{3+} + 4OH^- \rightleftharpoons AlO_2^- + 2H_2O$$
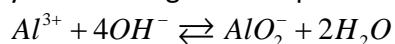
The AlO_2^- ion is the aluminate or metaaluminate ion. In some literature, the equation is written as:

$$Al^{3+} + 4OH^- \rightleftharpoons Al(OH)_4^-$$
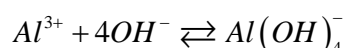
The two descriptions are equally valid. It was found practical to use the first of these expressions in the current project. At low pH, aluminum will mainly be present as Al^{3+}, at high pH as AlO_2^-. The pH dependence of this equilibrium is shown in Figure 1. At pH higher than 10.4, practically all aluminum is on the aluminate, AlO_2^- form. Below pH 9.2 practically all aluminum is present as aluminum ions, Al^{3+}.

One problem caused by the formation of the aluminate ion is that the computer program has to be prepared to deal with very small numbers. At low pH, the amount of aluminate ions can be less than 10^{-40}. At high pH, the amount of aluminum ion can become equally low.

The thermodynamic model used here requires the standard state chemical potential of the ionic species as input. The standard state chemical potential of the aluminate ion was found in the NIST databank to be -830.9 kJ/mol. It was found impossible to reach a reasonable modeling result using this value. The value was instead fitted to the experimental data and a value of -734.0 kJ/mol was instead used.
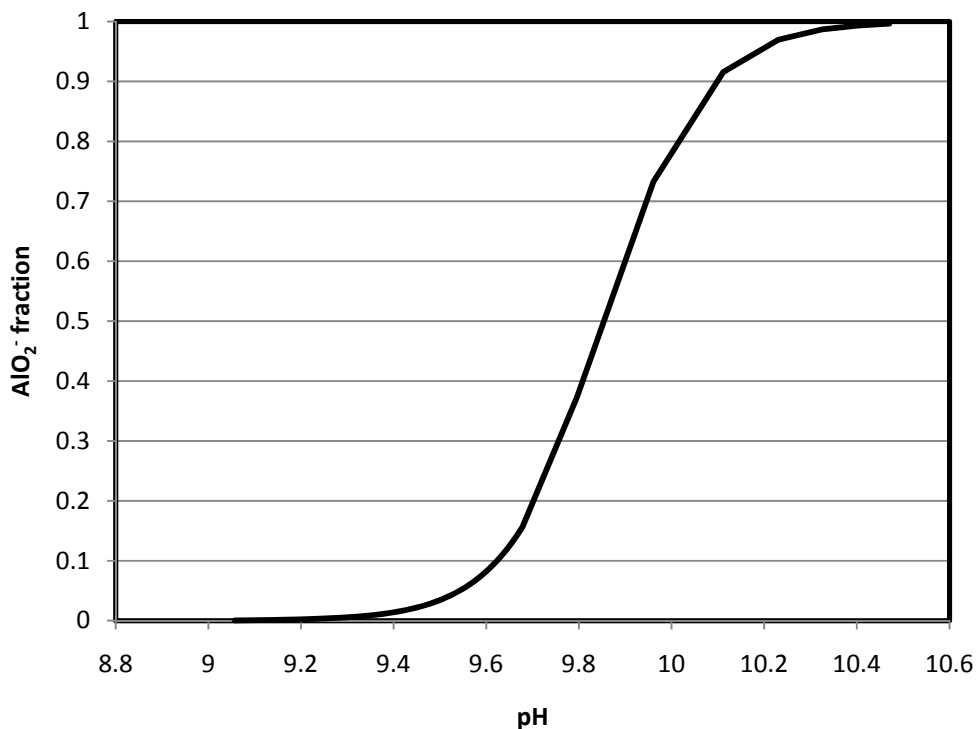
Figure 1: The fraction of aluminum ions present as aluminate ions as a function of pH. At pH higher than 10.4, practically all aluminum is on the aluminate, AlO_2^- form. Below pH 9.2 practically all aluminum is present as aluminum ions, Al^{3+}.

Experimental data used for modeling aluminum species

The experimental data used for determining model parameters for aluminum species are listed in Table 1. The types of data are mainly vapor pressure measurements of some sort and solid-liquid equilibrium (SLE) measurements.

As it was the case with fluorides, many of the experimental data for aluminum salts are scattered and show different tendencies.

Table 1: Sources and types of data used for determining model parameters for aluminum species.

Source	Type of data
Burge DE, Osmotic coefficients in aqueous solutions, studies with the vapor pressure osmometer, J. Phys. Chem., 67(1963)2590-3	Osmotic coefficients for Al_2SO_4 at 37°C
Robinson RA, The osmotic and activity coefficient data of some aqueous salt solutions from vapor pressure measurements, J. Am. Chem. Soc., 59(1937)84-90	Osmotic coefficients for Al_2SO_4 at 25°C
Smith NO, Walsh PN, Dissociation Pressures and Related Measurements in the System Aluminium	Al_2SO_4, boiling point temperatures of solutions

Sulfate-Water, J. Am. Chem. soc., 76(1954)2054-7	
Fricke R, Havestadt L, Verdünnungsarbeiten und Verdünnungsvärmen im Gebiet konzentrierter Lösungen, Z. Elektrochem., 33(1927)441-455	Water activity of $AlCl_3$ solutions at 0 and 15°C
Jauch K, Die specifische Wärme wässeriger Salzlösungen, Z. Phys., 4(1921)441-7	Heat capacity of $AlCl_3$ solutions at 18°C
Hovey JK, Tremaine PR, Thermodynamics of aqueous aluminium: standard partial molar heat capacities of aluminium(3+) from 10 to 55°C, Geochim. Cosmochim. Acta 50(1986)453-9	Heat capacity of $AlCl_3$ solutions containing various amounts of HCl at temperatures from 10 to 55°C
Jones HC, Pearce JN, Dissociation as measured by freezing point lowering and by conductivity - bearing on the hydrate theory, Am. Chem. J. 38(1907)683-743	Freezing point depression of $AlCl_3$ solutions.
Malquori G, I sistemi KCl-FeCl3-H2O e AlCl3-FeCl3-H2O fra 0° e 60°, Gazz. Chim. Ital., 58(1928)891-898	SLE of $AlCl_3$ at various temperatures.
Ts'ai, LS, Yen, WH, The system: aluminium sulphate-potassium sulphate-water, J. Chinese Chem. Soc., 4(1936)178-82	SLE of the Al2(SO4)3 – K2SO4 – H2O system.
Marino, L., Sulle condizioni di esistenza dei sali doppi Al2(SO4)3·K2SO4·8H2O e Al2(SO4)3(NH4)2SO4·8H2O. Loro correlatione coi corrispondenti solfati delle terre rare, Gazz. Chim. Ital., 35(1905)341-364	SLE of the Al2(SO4)3 – K2SO4 – H2O system.
Carter RH, Solubilities of some inorganic fluorides in water at 25°C, Ind. Eng. Chem., 20(1928)1195	SLE of AlF_3
Ehret WF; Frere FJ, Ternary Systems Involving water and Aluminium Fluoride with Aluminium Nitrate, Sulfate or Chloride, J. Am.Chem. Soc., 67(1945)68-71	SLE of AlF_3, $AlCl_3$, $Al_2(SO_4)_3$ and mixtures of AlF_3 with $Al_2(SO_4)_3$ and $AlCl_3$.
Horan HA, Skarulis JA, The system Li2SO4-Al2(SO4)3-H2O at 0 C, J. Am. Chem. Soc., 61(1939)2689-2691	SLE of $Al_2(SO_4)_3$
Smith NO, Walsh PN, Dissociation Pressures and Related Measurements in the System Aluminium Sulfate-Water, J. Am. Chem. Soc., 76(1954)2054-7	SLE of $Al_2(SO_4)_3$
Henry JL, King GB, The System Aluminium Sulfate-Sulfuric Acid-Water at 60 °C, J. Am. Chem. Soc. 71(1949)1142-4	SLE of $Al_2(SO_4)_3$ with H_2SO_4 in water.
Henry JL, King GB, Phase Rule Investigation of the	SLE of $Al_2(SO_4)_3$

System Al2O3-SO3-H2O at 60 C, Basic Region, J. Am. Chem. Soc., 72(1950)1282-6	
Skarulis JA, Horan HA, and Maleeny R, The Ternary System Na2SO4-Al2(SO4)3-H2O at 0°, J. Am. Chem. Soc., 76(1954)1450-1	SLE of the aqueous $Al_2(SO_4)_3$ – Na_2SO_4 system
Tananaev IV, On the ternary system AlF3-HF-H2O, Zhur. Obshch. Khim., 8(1938)1120-4	SLE of the AlF_3-HF-H_2O system
Seidel W, and Fischer W, Die Löslichkeit einiger Chloride und Doppelchloride in wässriger Salzsäure als Grundlage von Trennungen, Zeitschrift für anorganische und allgemeine Chemie, 247(1941)367-383	SLE of the $AlCl_3$-H_2O system
Taylor D, Bassett H, The system Al2(SO4)3-H2SO4-H2O, J. Chem. Soc., (1952)4431-4442	SLE of $Al_2(SO_4)_3$ with H_2SO_4 in water.
Bassett H, Goodwin TH, The basic Aluminium Sulphates, J. Chem. Soc., (1949)2239-2279	SLE of $Al_2(SO_4)_3$ with H_2SO_4 in water.
Occleshaw VJ, The equilibrium in the system aluminium sulphate-copper sulphate-water and aluminium sulphate-ferrous sulphate-water at 25°, J. Chem. Soc., 127(1925)2598-2602	SLE of $Al_2(SO_4)_3$ in water.
Malquori G, Il sistema AlCl3-KCl-H2O a 25 C, Atti. Accad. Lincei, 5(1927)510-511	SLE of the $AlCl_3$-KCl-H_2O system at 25°C
Malquori G, Parravano N, Il sistemi AlCl3-HCl-H2O, KCl.HCl-H2O e KNO3-HNO3-H2O a 25 C., Atti. Accad. Lincei, 5(1927)576-8	SLE of the $AlCl_3$-HCl-H_2O system at 25°C
Malquori G, Il sistema: AlCl3-FeCl3-KCl-H2O a 25°, Gazz. Chim. Ital., 59(1929)556-63	SLE of the $AlCl_3$-KCl-H_2O system at 25°C
Yatlov VS, Pinaevskaya, Equilibrium in the System AlF3 - H2O, Zhur. Obschei. Khim., 16(1946)27-32	SLE of the AlF_3 - H_2O system
Fricke R, Jucaitis P, Untersuchungen über die Gleichgewichte in den Systemen Al2O3·Na2O·H2O und Al2O3·K2O·H2O, Z. Anorg. Chem., 191(1930)129-149	SLE of the Al_2O_3 - Na_2O -·H_2O and the Al_2O3 - K_2O - H_2O systems
Yatlov VS, Pinaevskaya EH, Equilibrium in the system NaF-AlF3-H2O, Zhur. Obschei. Khim., 19(1949)24-31	SLE of the NaF-AlF_3-H_2O system
Schreinemakers FAH, de Waal AJC, Water, lithium sulfate en aluminiumsulfaat, Chem. Weekblad, 3(1906)539-543	SLE of $Al_2(SO_4)_3$ in water.
Dobbins JT, Addleston JA, A study of the soda-alum system. II., J. Phys. Chem., 39(1935)637-42	SLE of the aqueous $Al_2(SO_4)_3$ – Na_2SO_4 system

Reference	Description
Dobbins JT, Byrd RM, A study of the soda-alum system, J. Phys. Chem., 35(1931)3673-6	SLE of the aqueous $Al_2(SO_4)_3$ – Na_2SO_4 system
Caven RM, Mitchell TC, Studies of equilibrium in systems of the type Al2(SO4)3-M''SO4-H2O. Part I. Aluminium sulphate-copper sulphate-water and aluminium sulphate-manganous sulphate-water at 30°, J. Chem. Soc., 127(1925)527-31	SLE of $Al_2(SO_4)_3$ in water.
Sanders JP, Dobbins JT, The system: lithium sulphate-aluminium sulphate-water, J. Phys. Chem., 35(1931)3086-9	SLE of $Al_2(SO_4)_3$ in water.
Sarkarova R, Mironova ON, Solubility in the aluminium chloride-calcium chloride-lithium chloride system, Zh. Neorg. Khim., 35(1990)747-751	SLE of the $AlCl_3$ – $CaCl_2$ – H_2O system
Sarkarov RA, Mironova ON, Solubility in the aluminium chloride-lithium chloride-sodium chloride system, Zh. Neorg. Khim., 35(1990)280-2	SLE of the $AlCl_3$ – $NaCl$ – H_2O system
Malquori G, Il sistema AlCl3-HCl-H2O fra 0 e 80 C., Atti Accad. Lincei [6], 7(1928)740-744	SLE of the $AlCl_3$ – HCl – H_2O system
Malquori G, Il sistema AlCl3-KCl-H2O fra 0 e 80 C., Atti Accad. Lincei [6], 7(1928)745-747	SLE of the $AlCl_3$ – KCl – H_2O system
Lepeshkov IN, Danilov VP, Selin AN, Kim VP, Zaitseva LA, Gorbacheva NN, Solubility and solid phases in the H2SO4 - Na2SO4 - Al2(SO4)3 - H2O system at 50 C, Russ. J. Inorg. Chem., 32(1987)275-276	SLE of $Al_2(SO_4)_3$ with H_2SO_4 in water.
Mozgovykh GYa, Nurkeev SS, Romanov LG, Zaripova AG, Eremin NI, Calcium sulfate solubility in aluminium sulfate aqueous solutions at 25, 50, 75 and 90°, J. Appl. Chem. USSR, 57(1984)1946-1948	SLE of $Al_2(SO_4)_3$ with $CaSO_4$ in water.
Chibizov VP, Moshinskii AS, Geger VYa, Solubility of calcium sulfate in aqueous solutions of aluminium sulfate at 75.deg, J. Appl. Chem. USSR, 48(1975)2353-4	SLE of $Al_2(SO_4)_3$ in water.
Moshinskii AS, Chibizov VP, Polytermic 0-100.deg. diagram of solubility and double sulfate in the magnesium sulfate-aluminium sulfate-water system., J. Appl. Chem. USSR, 48(1975)2256-9	SLE of $Al_2(SO_4)_3$ in water.
Chibizov VP, Moshinskii AS, M2(SO4)-H2SO4-H2O systems (M=aluminium, gallium, indium) at 25°, Russ. J. Inorg. Chem, 28(1983)1361-3	SLE of $Al_2(SO_4)_3$ with H_2SO_4 in water.

Petrov, MR, Roslyakova ON, Blau TV, The Al(NO3)3-Al2(SO4)3-H2O system at 25°C, Russ. J. Inorg. Chem., 27(1982)1534-5	SLE of $Al_2(SO_4)_3$ in water.
Ashchyan TO, Itkina LS, Danilov VP, Lepeshkov IN, Kotova LT, 25°C Solubility isotherm of the Al, Li//OH, SO4-H2O system, Russ. J. Inorg. Chem., 23(1978)448-454	SLE of $Al_2(SO_4)_3$ in water.
Karnaukhov AS, Fedorenko TP, Shevchuk VG, Cadmium sulfate-aluminium sulfate-water system at 25.deg., Russ. J. Inorg. Chem., 18(1973)152	SLE of $Al_2(SO_4)_3$ in water.
Shevchuk VG, Lebedinskii BN, The Al2(SO4)3-Li2SO4-H2O system, Russ. J. inorg. Chem, 12(1967)582-3	SLE of $Al_2(SO_4)_3$ in water.
Zapol'skii AK, Sazhin VS, Shameko GS, Rybachuk FYa, Solubility of aluminium sulfate in the aluminium sulfate-water system, Ukr. Khim. Zh., 40(1974)40-3	SLE of $Al_2(SO_4)_3$ with H_2SO_4 in water.
Holldorf H, Barnekow U, Petzold D, Schure W, Die isothermen AlCl3·6H2O - Sättigungsflächen der Systeme AlCl3 - MgCl2 - HCl und AlCl3 - KCl - H2O bei 40 °C, 55°C, 70°C und 85°C, Freiberg. Forschungsh. A, 671(1983)35-55	SLE of the $AlCl_3$ – HCl – KCl - H_2O system
Holldorf H, Wahl G, Studies on the aluminium chloride-water and aluminium chloride-hydrochloric acid-water systems, Freiberg. Forschungsh. A, 671(1983)26-34	SLE of the $AlCl_3$ – HCl – H_2O system
Britton HTS, The system potassium sulphate-aluminium sulphate-water at 25°, J. Chem. Soc., 121(1922)982-986	SLE of the aqueous $Al_2(SO_4)_3$ – K_2SO_4 system
Brown RR, Daut GE, Mrazek RV, Gokcen NA, Solubility and activity of aluminium chloride in aqueous hydrochloric acid solutions, Rep. Invest., Bureau Mines, 8379(1979)1-17	SLE of the $AlCl_3$ – HCl – H_2O system
Shevchuk VG, Romanov OA, The Al2(SO4)3-(NH4)2SO4-Na2SO4-H2O system at 25°C, Russ. J. Inorg. Chem., 16(1971)1526-7	SLE of the aqueous $Al_2(SO_4)_3$ – Na_2SO_4 system
Druzhinin, IG, Manakunov B, Kuznetsov VG, Solubility in the aqueous aluminium, sodium, nickel, sulphate quaternary system, Russ. J. Inorg. Chem., 6(1961)1304-8	SLE of the aqueous $Al_2(SO_4)_3$ – Na_2SO_4 system
Sveshnikova VN, Solubility in the ternary system Al2O3-P2O5-H2O at 90°C, Russian Journal of	SLE of the Al_2O_3-P_2O_5-H_2O system

Inorg. Chem., 5(1960)227-229	
Khripin LA, Lepeshkov IN, Physicochemical Investigation of the K2SO4-CsSO4-Al2(SO4)3 -H2O system at 50 °C,Russian Journal of Inorg. Chem., 5(1960)230-235	SLE of the aqueous $Al_2(SO_4)_3 - K_2SO_4$ system
Farelo F, Fernandes C, and Avelino A, Solubilities for Six Ternary Systems: NaCl + NH4Cl + H2O, KCl + NH4Cl + H2O, NaCl + LiCl + H2O, KCl + LiCl + H2O, NaCl + AlCl3 + H2O, and KCl + AlCl3 + H2O at T = (298 to 333) K, J. Chem. Eng. Data, 50(2005)1470-1477	SLE of the $AlCl_3 - KCl - H_2O$ and the $AlCl_3 - NaCl - H_2O$ systems
Du C, Zheng S, Zhang Y, Phase equilibria in the K2O-Al2O3-H2O system at 40°C, Fluid Phase Equilibria, 238(2005)239-241	SLE of the $K_2O-Al_2O_3-H_2O$ system
Li Z and Demopoulos GP, Effect of NaCl, MgCl2, FeCl2, FeCl3, and AlCl3 on Solubility of CaSO4 Phases in Aqueous HCl or HCl + CaCl2 Solutions at 298 to 353 K, J. Chem. Eng. Data, 51(2006)569-576 (2)	SLE of the $CaSO_4 - AlCl_3 - H_2O$ system
Brosheer JC, Lenfesty FA, Anderson JF Jr, Solubility in the System Aluminum Phosphate-Phosphoric Acid-Water, J. Am. Chem. Soc., 76(1954)5951-5956	SLE of the $Al_2O_3-P_2O_5-H_2O$ system
Martin R; DucMauge C; Guerin H, Aluminum phosphates: equilibrium diagram for the system Al2O3-P2O5-H2O at 60°C, Bulletin de la Societe Chimique de France, (1960)851-856	SLE of the $Al_2O_3-P_2O_5-H_2O$ system
Jameson RF; Salmon JE, Aluminum phosphates; phase-diagram and ion-exchange studies of the system Al2O3-P2O5-H2O at 25 °C, Journal of the Chemical Society, (1954)4013-17	SLE of the $Al_2O_3-P_2O_5-H_2O$ system
Gayer KH, Thompson LC, and Zajicek OT, The Solubility of Aluminum Hydroxide in Acidic and Basic Media at 25°, Canadian Journal of Chemistry, 36(1958)1260-1267 (9)	SLE of the $K_2O-Al_2O_3-H_2O$ system
Sprauer JW, Pearce DW, Equilibria in the Systems Na2O–SiO2–H2O and Na2O–Al2O3–H2O at 25°C, J. Phys. Chem., 44(1940)909-916	SLE of the $Na_2O-Al_2O_3-H_2O$ system
Jucaitis P, Über die Zusammensetzung und Konstitution der Alkalialuminate. Sind die Aluminate Hydroxoverbindungen?, Z. anorg. Chem., 220(1934)257-267	SLE of the $Na_2O-Al_2O_3-H_2O$ system

Volf FF, Kuznetsov SI, Polytherms in the Al2O3 - Na2O - H2O System, Journal of Applied Chemistry of the USSR, 28(1955)565-569	SLE of the Na_2O-Al_2O_3-H_2O system
Goudriaan F, The aluminates of sodium. Equilibria in the system Na2O-Al2O3-H2O, Recueil des Travaux Chimiques des Pays-Bas et de la Belgique, 41(1922)82-95	SLE of the Na_2O-Al_2O_3-H_2O system
Bassett H, and Watt W, Pickeringite and the System MgSO4-Al2(SO4)3-H2O, Journal of the Chemical Society (Resumed), (1950)1408-1414	SLE of $Al_2(SO_4)_3$ in water.

Results

Systems with chloride

The modeling results for systems with aluminum chloride are relatively good. There were no particular problems with the experimental data. The solubility of $AlCl_3$ at temperatures between minus 50 and plus 100 degrees is shown in Figure 2. The experimental data are plotted as circles on the calculated graph. The stable form of AlCl3 at these temperatures is $AlCl_3 \cdot 6H_2O$.
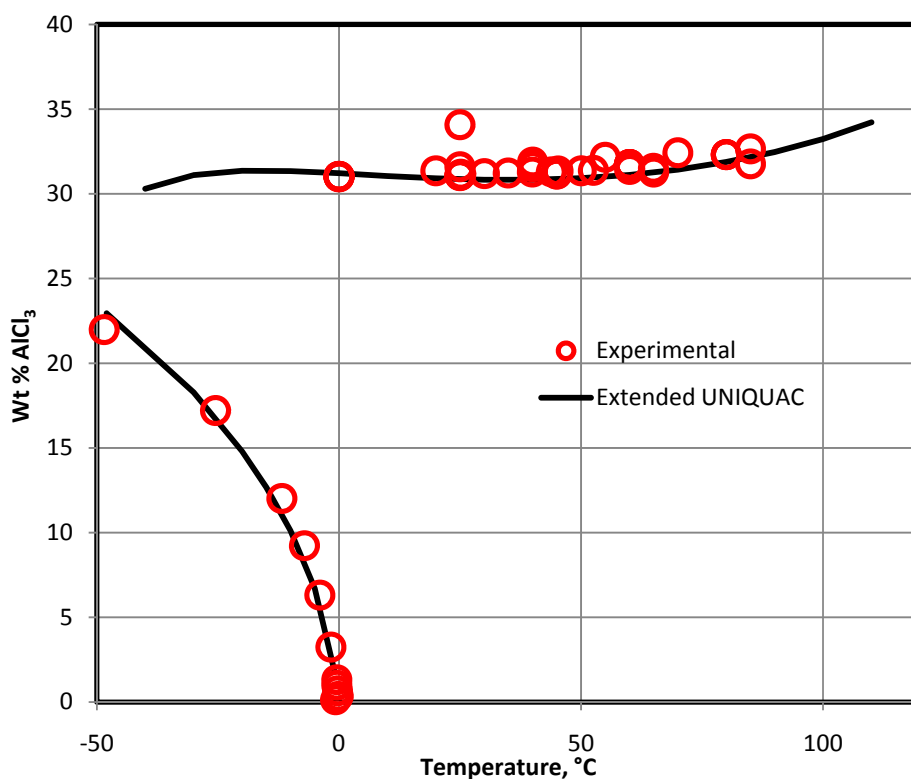
Figure 2: The solubility of $AlCl_3$ as a function of temperature.

The phase diagram for the $AlCl_3$ – $NaCl$ – H_2O system at 25°C is shown in Figure 3. The experimental data come from two different sources, but there is apparently a good agreement between the two sets of data.
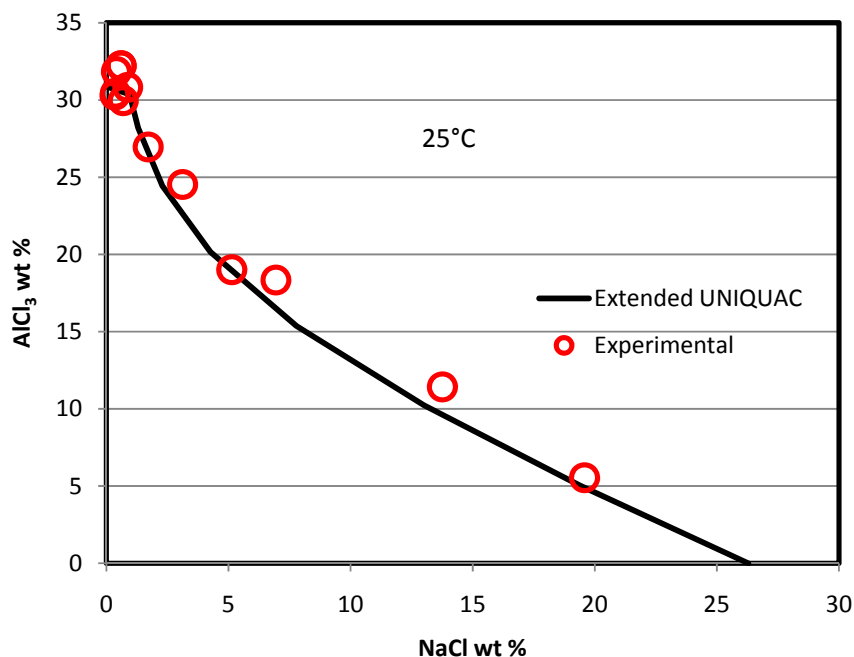
Figure 3: Phase diagram for the AlCl3 – NaCl – H2O system at 25°C

An example of the calculation of the phase behavior of the $AlCl_3$ – KCl – H_2O system at 40°C is shown in Figure 4. In this system, the experimental data are a little scattered at some temperatures. But the modeling result is generally good anyway. Data for $AlCl_3$ – KCl – HCl - H_2O were also modeled with great accuracy. An example of a calculated phase diagram for this system is shown in Figure 5, which is valid at 70°C. The phase diagram in Figure 5 does not show the water content but only the salt composition. This quaternary system would require one more dimension for displaying all concentrations.

The experimental data and the phase diagram line in Figure 5 show salt compositions in solutions that are simultaneously saturated with $AlCl_3·6H_2O$ and KCl. Corresponding data at other temperatures were also available for this system. These temperatures are 40, 55, and 85°C.

The solubility of $AlCl_3·6H_2O$ in solutions containing HCl is shown in Figure 6. The solubility of $AlCl_3·6H_2O$ is reduced significantly by the addition of HCl.
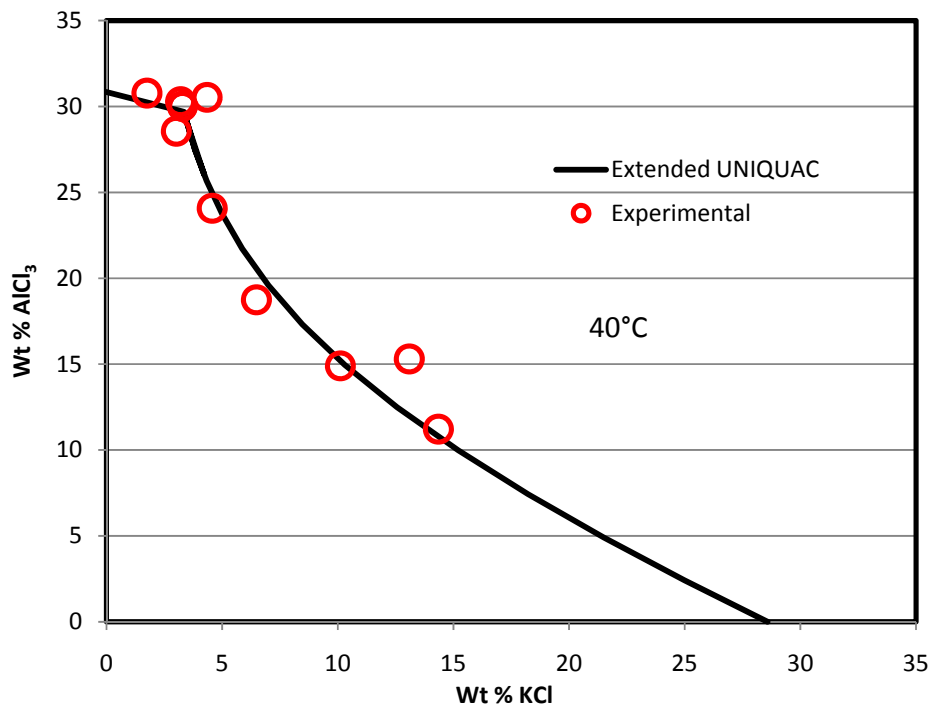
Figure 4: Phase diagram for the AlCl3 – KCl – H2O system at 40°C
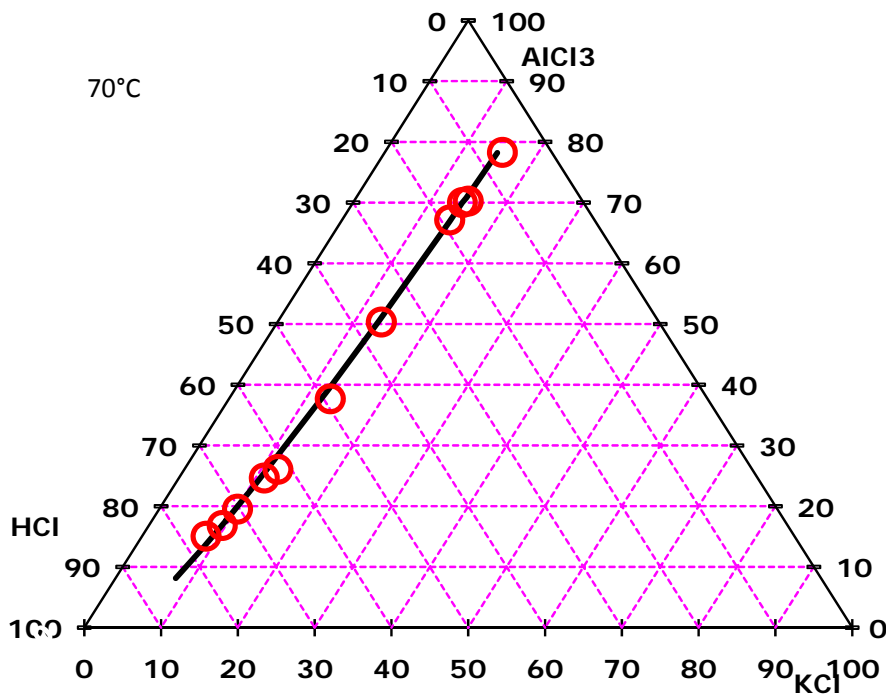
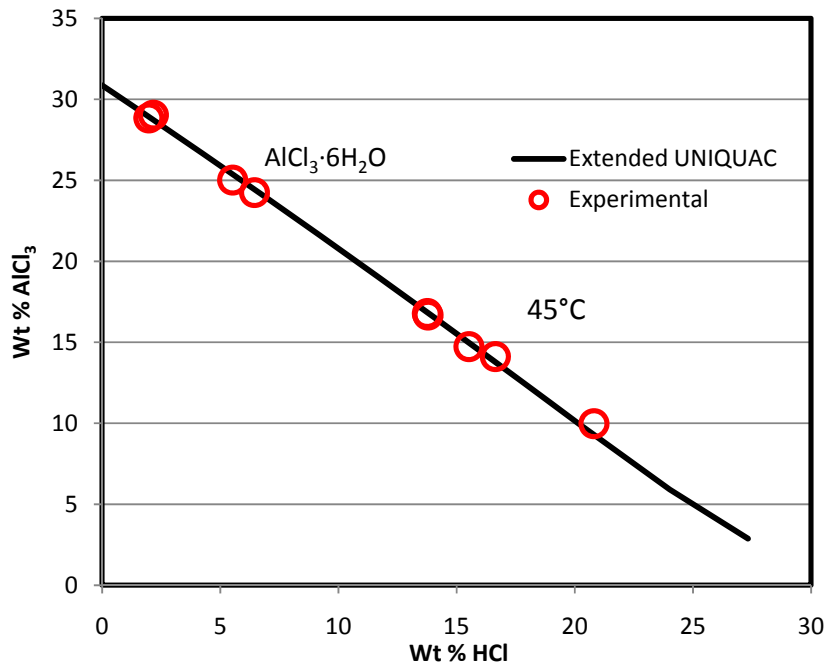**Figure 5: Phase diagram for the AlCl$_3$ – KCl – HCl – H$_2$O system at 70°C.**

Figure 6: The solubility of AlCl₃·6H₂O is reduced significantly by the addition of HCl. This is the "common ion effect". This tendency is described accurately by the model as shown in this phase diagram at 45°C.
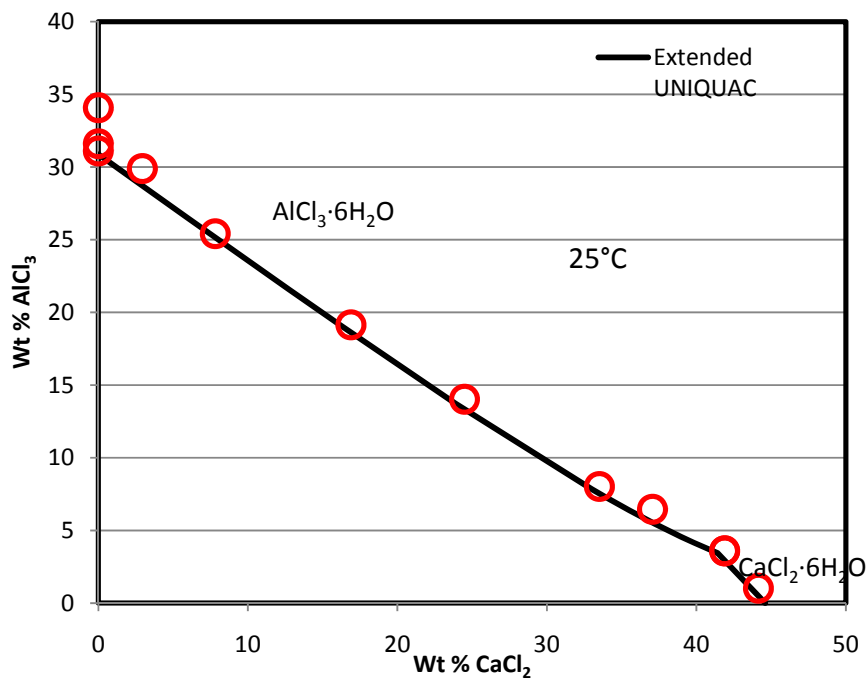

Figure 7: Solubility in the AlCl₃ – CaCl₂ – H₂O system at 25°C
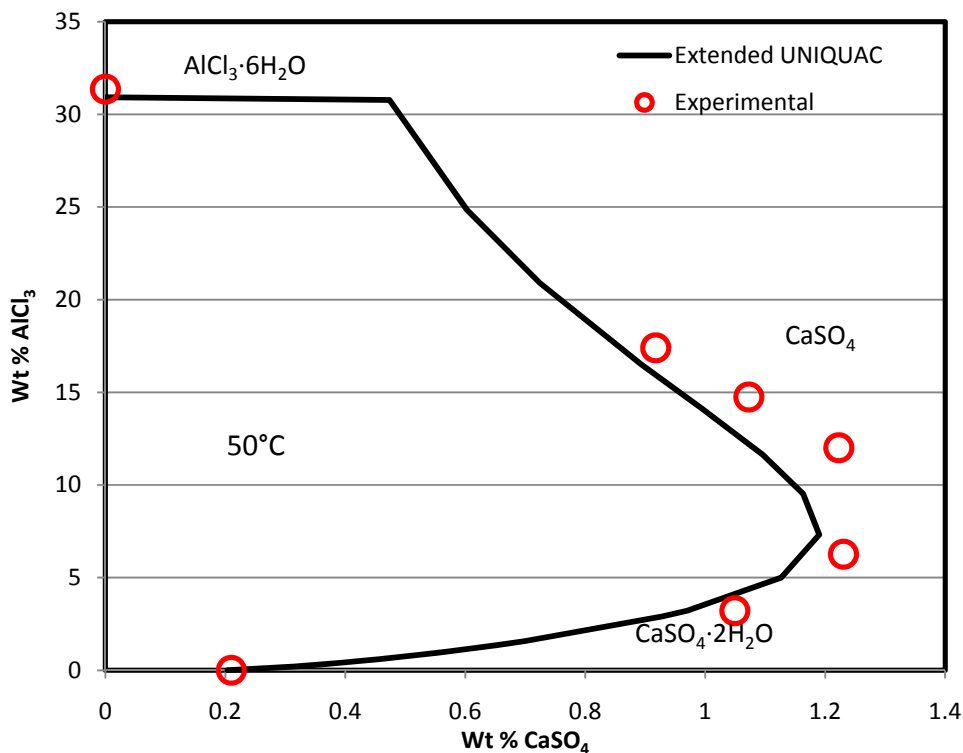
Figure 8: The solubility of CaSO$_4$ in solutions with AlCl$_3$ at 50 °C.

As illustrated in Figure 8, the solubility of AlCl₃ is not influenced by the addition of CaSO₄. But on the other hand, the solubility of CaSO₄ is significantly increased by the addition of AlCl₃ to the solutions. Experimental data for this system are available at 25, 50 and 80°C. The tendency seen in Figure 8 is also found at 25 and 80°C. While the model and the experimental data agree well at 25 and 50°C, there is more difference at 80°C. According to the experimental data, the solubility of CaSO₄ is increased further at 80°C, while according to the model, the solubility of CaSO₄ is increased less at 80°C. According to the model the solubility increase of CaSO₄ caused by AlCl₃ goes through a maximum somewhere between 50 and 80°C.

Systems with fluoride

The modeling results for systems with fluoride are not as good as those for systems with chloride. The reason might be that Aluminum has a tendency to form complexes like AlF_4^- in solutions containing fluoride at low pH. The stable form of AlF$_3$ at the relevant temperatures is AlF$_3$·3H$_2$O. The solubility of AlF$_3$ in pure water is calculated as accurately as possible by the model considering the scattering of the data. This is shown in Figure 9.
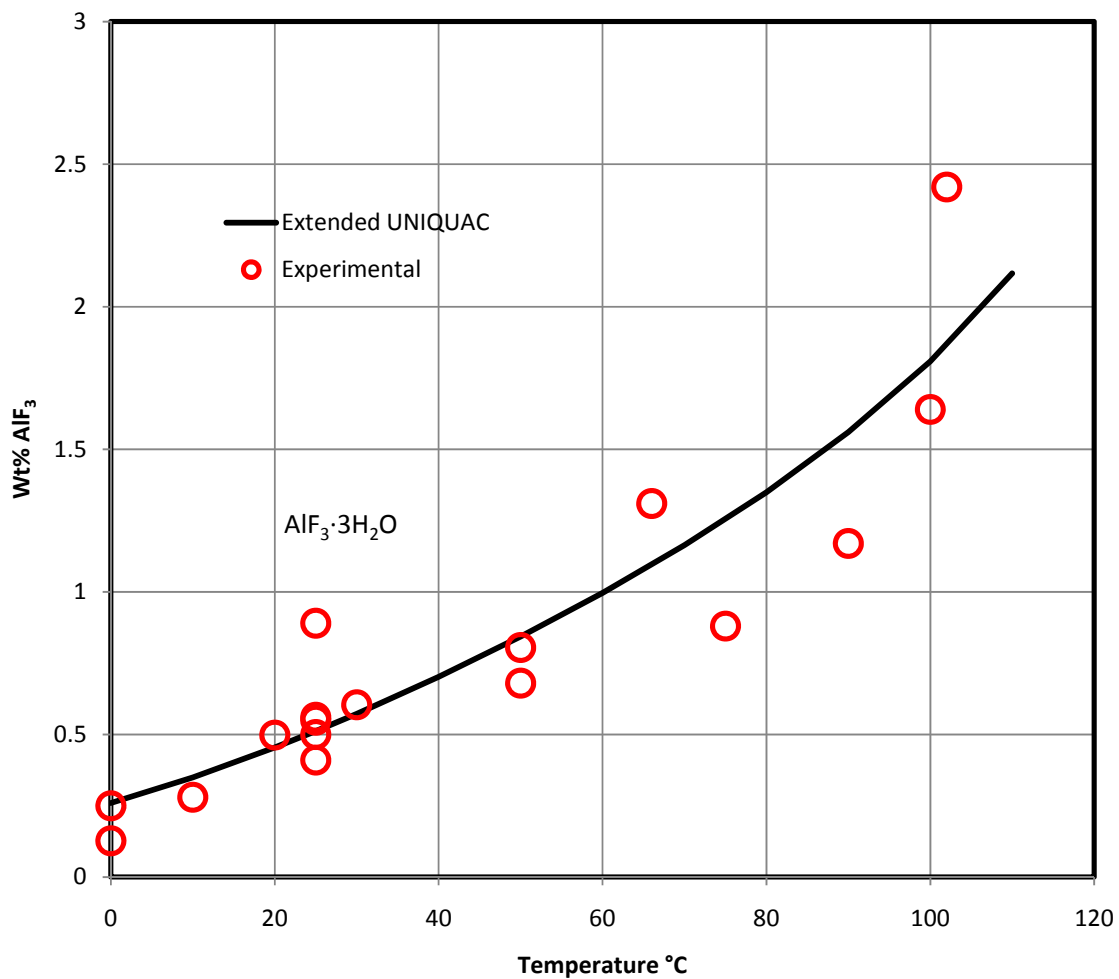
Figure 9: The solubility of AlF3 in water. The solid phase is AlF$_3$·3H$_2$O at all the temperatures considered here.

The solubility of AlF3 in solutions containing HF or HCl is not reproduced well by the model. There were not sufficient experimental data to properly model systems with AlF$_3$ together with sulfuric acid or sulfates. It is not known if double salts are forming in these systems.

Systems with sulfate.

Many experimental data are available for aqueous systems containing $Al_2(SO_4)_3$. $Al_2(SO_4)_3$ has a tendency to form hydrates and hydrated double salts. Potassium alum (or potash alum) is $KAl(SO_4)_2 \cdot 12H_2O$. Sodium alum and other alums haves similar chemical formulae. One problem is that investigators do not agree on the various types of hydrates formed in these systems. In their paper Henry and King[1] discussed the validity of the 55 different reported solids in the $Al_2O_3 - SO_3 - H_2O$ system.

In this project, it will be assumed that the stable form of precipitated $Al_2(SO_4)_3$ contains 18 hydrate water as $Al_2(SO_4)_3 \cdot 18H_2O$. The calculated phase diagram for $Al_2(SO_4)_3$ in water is shown in Figure 10. The data are slightly scattered and many of these data were reported as being with 19, 12, 16, or 17 hydrate water instead of 18.
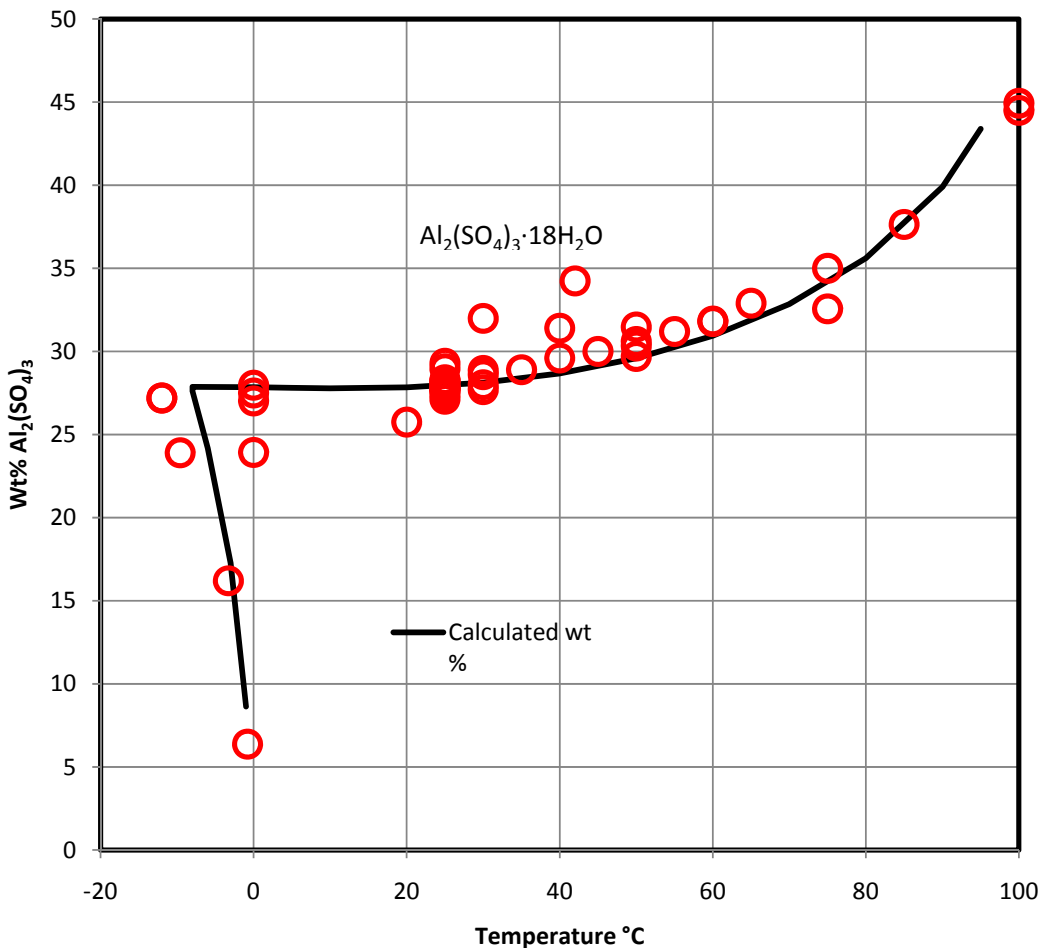
Figure 10: The solubility of $Al_2(SO_4)_3$ in water. The solid phase is $Al_2(SO_4)_3 \cdot 18H_2O$ at all temperatures.

[1] Henry JL, King GB, Phase Rule Investigation of the System Al2O3-SO3-H2O at 60 C, Basic Region, J. Am. Chem. Soc., 72(1950)1282-6

The calculated phase diagram for the $Al_2(SO_4)_3$ - Na_2SO_4 - H_2O system is shown in Figure 11 for 25°C. At other temperatures, the data are more scattered. Some data from the 0°C isotherm were obviously meta-stable solutions rather than true equilibrium data.
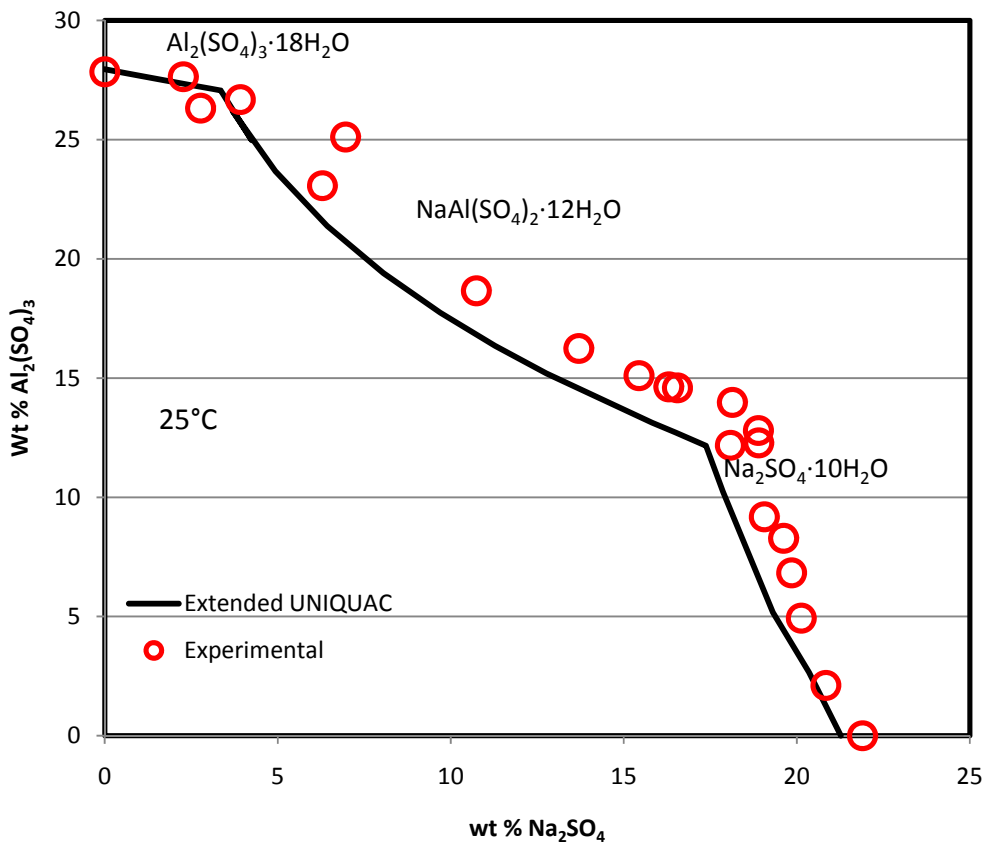

Figure 11: Solubility in the aqueous aluminum sulfate – sodium sulfate system at 25 °C. The double salt NaAl(SO₄)₂·12H₂O is sodium alum.

The phase diagram in Figure 12 shows the 0°C isotherm for the $Al_2(SO_4)_3$ - K_2SO_4 - H_2O system. By comparison of Figure 11 and Figure 12 it is very clear that the two otherwise similar systems behave quite differently. Potash alum has a relatively low solubility. By addition of a little K_2SO_4 to a solution containing $Al_2(SO_4)_3$, Potash alum, $KAl(SO_4)_2 \cdot 12H_2O$ will precipitate. The same happens if a small amount of $Al_2(SO_4)_3$ is added to a solution containing K_2SO_4. The solubility of potash alum increases with temperature. A few experimental data were available at 80°C. The best agreement between calculated and experimental data was found at 0°C. Particularly at 50°C, there are some differences between calculated and experimental data.
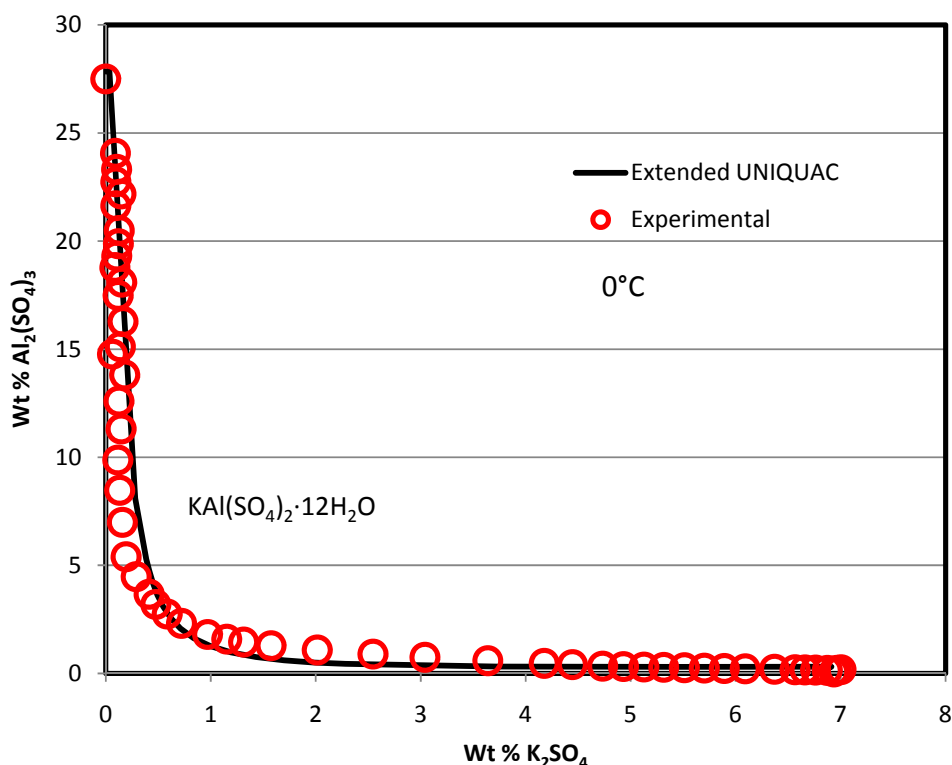
Figure 12: Solubility in the aqueous aluminum sulfate – potassium sulfate system at 0 °C. The double salt $KAl(SO_4)_2 \cdot 12H_2O$ is potassium (potash) alum.

The solubility of $Al_2(SO4)_3$ is influenced significantly by the addition of H_2SO_4. This is shown in the phase diagram in Figure 13. Some divergence between calculated and experimental data is seen. The number of data at this and other temperatures is limited. It was therefore not possible to get a better agreement. At sulfuric acid concentrations above 47 wt % a double salt, $Al_2(SO_4)_3 \cdot H_2SO_4 \cdot 12H_2O$ is formed.

The reduction in the solubility of $Al_2(SO4)_3$ is caused by the "common ion effect". The addition of sulfuric acid gives higher concentrations of the common sulfate ions. You could also say that $Al_2(SO4)_3$ is being "salted out" by the addition of sulfuric acid.
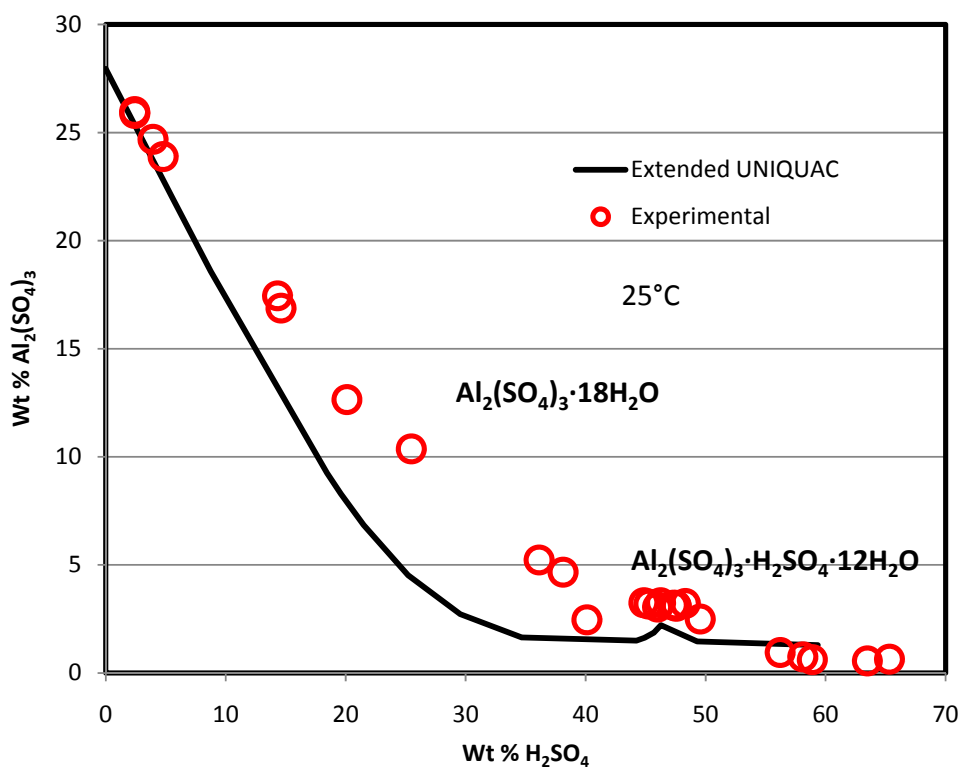
Figure 13: Solubility of $Al_2(SO_4)_3 \cdot 18H_2O$ as it is influenced by the addition of sulfuric acid. This is "salting out" of $Al_2(SO_4)_3 \cdot 18H_2O$ by H_2SO_4 or "common ion effect".

Hydroxide systems

According to Gayer et al.[2] the solubility of $Al(OH)_3$ in water is less than 30 micromols per kg water. Because of the formation of the aluminate ion, AlO_2^-, the apparent solubility of aluminum hydroxide is much higher at increased pH. Figure 14 shows the solubility in the $Al(OH)_3 - NaOH - H_2O$ system at 30°C. The solubility of aluminum hydroxide increases to more than 35 wt % and at the maximum solubility, the double salt $Na_2O \cdot Al_2O_3 \cdot 2\frac{1}{2}H_2O$ starts forming. This double salt is the only other stable solid in this ternary system. The same tendency as described in the isotherm at 30°C is seen also in the isotherms at 25, 45, 60, 80, and 95°C at which data were available.
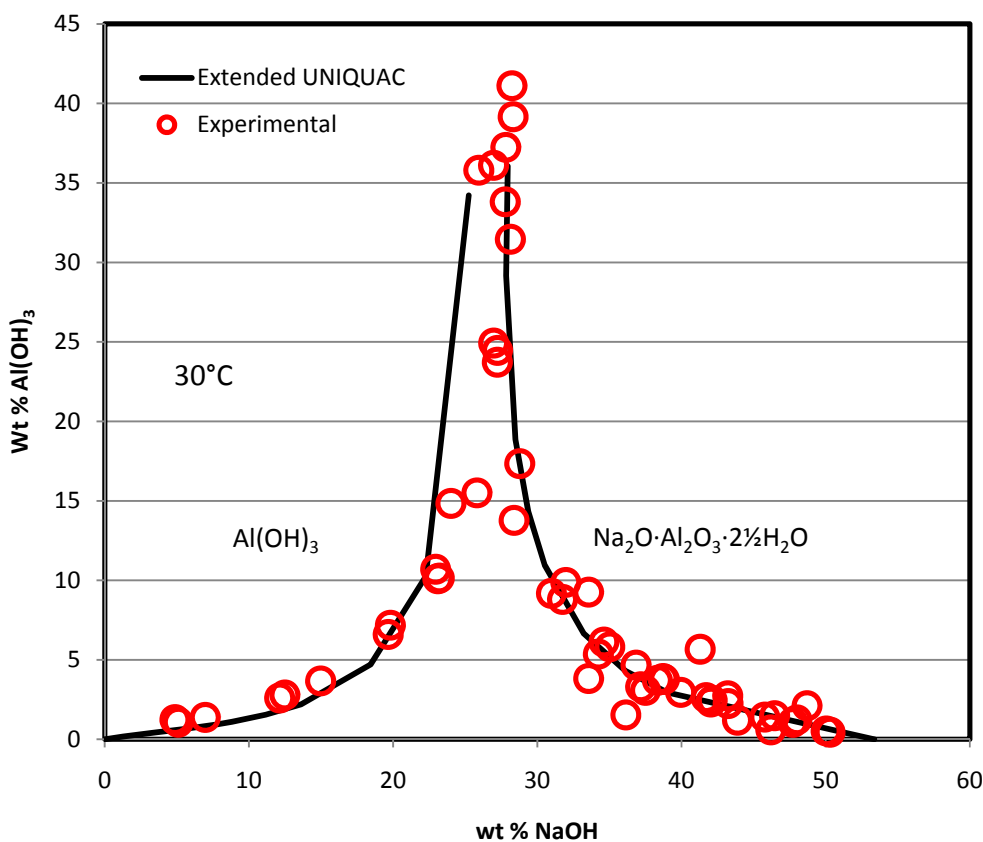

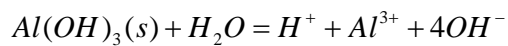**Figure 14: Solubility in the Al(OH)3 – NaOH – H2O system at 30°C.**

[2] Gayer KH, Thompson LC, and Zajicek OT, The Solubility of Aluminum Hydroxide in Acidic and Basic Media at 25°, Canadian Journal of Chemistry, 36(1958)1260-1267 (9)

The phase behavior of the Al(OH)$_3$ – KOH – H$_2$O system is similar to that of the sodium equivalent. The 40°C isotherm for this system is shown in Figure 15. At concentrations above 35% KOH, the stable solid phase is 2KOH·Al$_2$O$_3$·2H$_2$O.

The reason why the calculated phase diagram is not competed is that a singularity is appearing in the set of equations used for calculating the solubility of Al(OH)$_3$. The equations being solved are:

$$Al(OH)_3(s) = H_2O + AlO_2^- + H^+ \quad (1)$$

$$AlO_2^- + 2H_2O = Al^{3+} + 4OH^- \quad (2)$$

$$H_2O = H^+ + OH^- \quad (3)$$
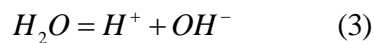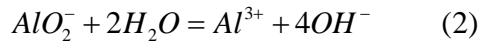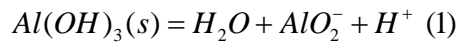
By addition of equations (1) and (2) one obtains

$$Al(OH)_3(s) + H_2O = H^+ + Al^{3+} + 4OH^-$$

Apparently, this equation contains also equation (3), which shows that the three equations are not linearly independent. Only two of these equations are required for solving the problem. To solve this problem, it might be necessary to make a change in the program.
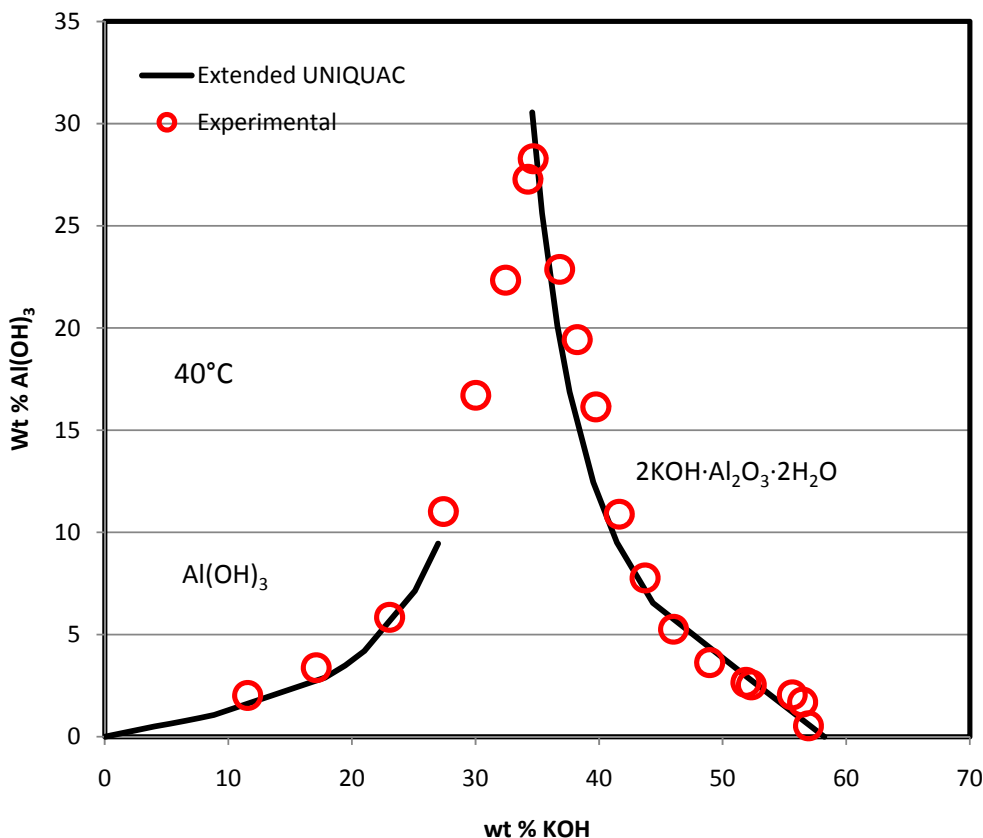

Figure 15: The 40°C solubility isotherm for the Al(OH)$_3$ – KOH – H$_2$O system

Phosphate systems

The experimental data for the phosphate systems with aluminum are contradictory. There is no agreement on which solid phases appear in the systems. It was therefore very difficult to model these systems and it might be necessary to remodel this sub system if more experimental data become available. There is for example not agreement on whether or not a dialuminumphosphate, $Al_2(HPO_4)_3$ exists or not. Some investigators found that when adding phosphoric acid to aluminum hydroxide, you will first see aluminum phosphate as $AlPO_4 \cdot 2H_2O$ precipitating. At a certain concentration of phosphoric acid, the stable phase will be $Al(H_2PO_4)(HPO_4) \cdot 3H_2O$, at even higher concentration of H_3PO_4 the solid salt will be $Al(H_2PO_4)(HPO_4) \cdot H_2O$. Finally, monoaluminumphosphate, $Al(H_2PO_4)_3$ is the stable solid phase. Others found actually a dialuminumphosphate precipitating also.

The disagreement between the experimental data makes it very difficult to model the system. In Figure 16, a solubility isotherm in the $Al(OH)_3 - H_3PO_4 - H_2O$ system is shown. $AlPO_4 \cdot 2H_2O$ is precipitating in solutions with up to 50 wt % H_3PO_4, which means solutions with pH lower than 2. In comparison, $Ca_3(PO_4)_2$ precipitates at much higher pH. It means that the solubility of $AlPO_4 \cdot 2H_2O$ is very low, and it might be challenging to remove aluminum from phosphate that has been precipitated with aluminum.
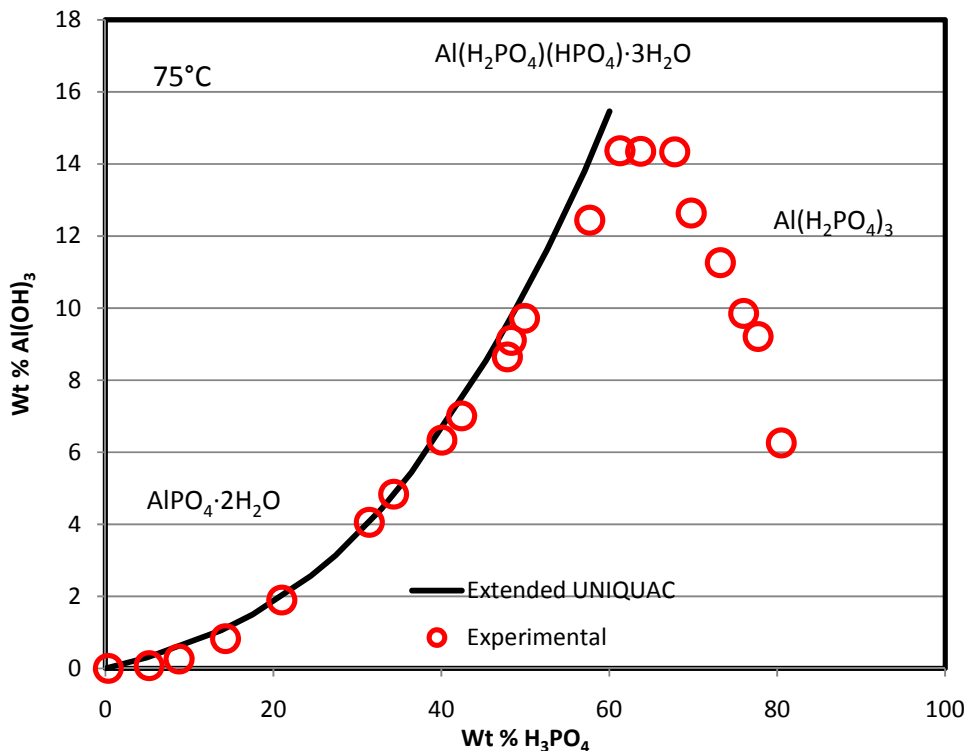

Figure 16: The solubility isotherm at 75°C in the AlOH)$_3$ – H$_3$PO$_4$ – H$_2$O system.

Conclusion

The aluminum ion has been added to the model by determining model parameters from experimental data. Because of particularities of the aluminum ion, systems with fluoride at low pH could not be modeled with high accuracy. Systems with phosphate also caused particular problems. Trialuminumphosphate, $AlPO_4 \cdot 2H_2O$ is extremely insoluble compared to for example $Ca_3(PO4)_2$. The removal of aluminum from phosphate precipitated as aluminumsalts can therefore be challenging. Numerical problems caused difficulties in calculating the complete phase diagram for the highly alkaline systems where aluminum hydroxide has large solubility.

Systems containing aluminum with chloride and sulfate could be modeled with good accuracy.