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Experimental Determination of the Stability of Aluminum-Fluoride Complexes to 300 °C in Near-Neutral and Alkaline Solutions

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Field observations (Moine, 1998, Zaraisky, 1995) and experimental modeling (Sanjuan and Michard, 1987; Zaraisky, 1994) demonstrate that aluminum mobility is markedly enhanced in aqueous solutions enriched in dissolved fluoride. Stability constants for the complexes formed between Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, and F^- have been determined by Baumann (1969), Couturier (1986), and Zaraisky (1994). However, despite this $Al(OH)_4^-$ and to a less extent $Al(OH)_3^0$ are the most abundant aqueous aluminum species in the absence of complexing ligands, very few studies have until now investigated their complexation with fluorine. The present study is aimed at filling this gap via the experimental determination of the stability of Al-F complexes in near-neutral and alkaline hydrothermal solutions.

Boehmite solubility was measured as a function of NaF concentration at temperatures from 90 to 300°C and P_{sat} in NH_4OH-NH_4Cl-(NaCl) solutions. Experiments were performed in stainless steel (at 200 and 300°C) and titanium (at 90, 150 and 200°C) autoclaves, both allowing sampling during experiments. Boehmite was synthesized from pure synthetic gibbsite as described in Castet et al. (1993). Solutions sampling started a few days after attainment of thermal equilibrium. During sampling, solutions were first filtered in situ (at run temperature) through titanium and a second time (at 25^{0}C) with a nitrate filter. Concentration of dissolved aluminum was determined by flameless Atomic Adsorption Spectroscopy. Analyses for fluorine were performed either with a fluoride-selective electrode or by ion chromatography. Values of pH were measured in situ at 90°C with a combined glass pH electrode or calculated at other temperatures using thermodynamic properties of the components of the system from SUPCRT92.

Comparison of boehmite solubility data with and without added fluoride demonstrates strong Al-F complexation. Analysis of pH and pF dependence of boehmite solubility indicates that the $Al(OH)_2F_2^-$ complex dominates Al speciation in fluoride-rich neutral and alkaline solutions. The equilibrium constant for the reaction

$$Al(OH)_4^- + 2F^- = Al(OH)_2F_2^- + 2OH^-$$

has been derived from experimental solubility data for concentrations of NaF to 0.01 m. At higher NaF molalities decrease of Al and F concentrations with time reflected formation of a new fluoride-bearing solid phase. Based on $Al(OH)_2F_2^-$ stability constants determined in the present study, we have reported on the figure plots figure 1 at 150 and 300°C of pH vs. pF showing the fields of predominance of Al aqueous species. It can be seen that the predominance field of $Al(OH)_2F_2^-$ expands towards lower pH values as the temperature increases. This results from the expansion of $Al(OH)_4^-$ domain at the expense of $Al(OH)_3^0$. Although the stability of $Al(OH)_2F_2^-$ increases with temperature, there is no appreciable change in the boundary between $Al(OH)_4^-$ and $Al(OH)_2F_2^-$ predominance fields. Thermodynamic calculations based on the results of the present study demonstrate that the presence of fluorine at concentrations as low as 1 ppm can greatly enhance aluminum mobility in most hydrothermal solutions.

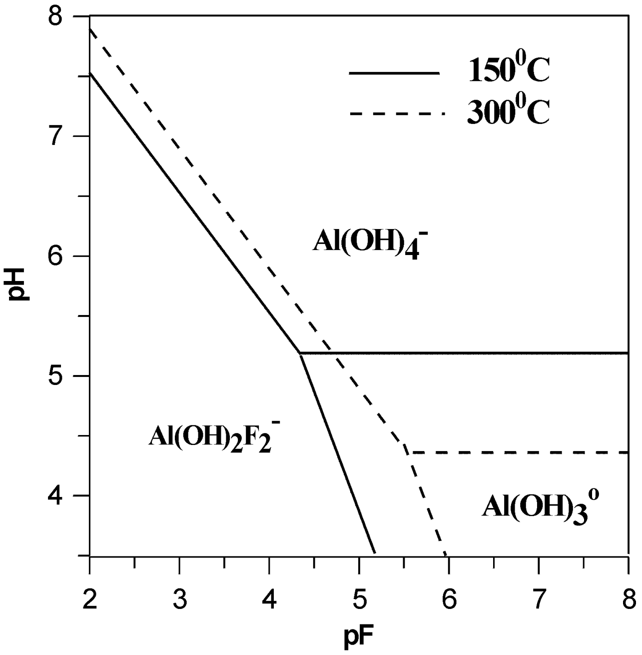

Figure 1: Predominance fields of aqueous species of Al

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