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## FLUORITE'S PRECIPITATION IN KOH SOLUTIONS IN VIEW OF REMOVING FLUORIDES FROM WASTEWATERS

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The process under study aims at removing dissolved fluorides from effluent waters through the addition of calcium and the precipitation of fluorite in a fluidized bed. In the concept developed at COMURHEX, the effluent is a highly concentrated KOH solution and the calcium is provided as a suspension of portlandite with calcite as an impurity. COMURHEX's target is to achieve an efficient defluorination of KOH solutions prior to recycling and to control the growth of the fluorite grains. Since building a fluorite crystallisation model requires a thermodynamic basis, we started exploring portlandite, calcite and fluorite solubility in concentrated KOH solutions.

We are primarily concerned with equilibria in the system  $\text{Ca}(\text{OH})_2\text{-CaCO}_3\text{-CaF}_2\text{-KOH-H}_2\text{O}$  at temperatures  $15 - 35^\circ\text{C}$  in KOH solutions up to 6M (340g/kg). Suspensions and mixtures are prepared in a 3 L stirred reactor under  $\text{N}_2$  atmosphere and the temperature is varied. Liquid samples are taken from the reactor, filtered, diluted, and analysed by ICP-AES for cations and ionic chromatography for anions, while the solids are washed in ethanol and observed by SEM.

In order to choose materials and improve techniques, this work was started with the  $\text{Ca}(\text{OH})_2\text{-CaCO}_3\text{-KOH-H}_2\text{O}$  subsystem, where solubility data and speciation models are already available from the literature [1]. In this subsystem we experienced the analytical and kinetic difficulties already quoted by other authors [2].

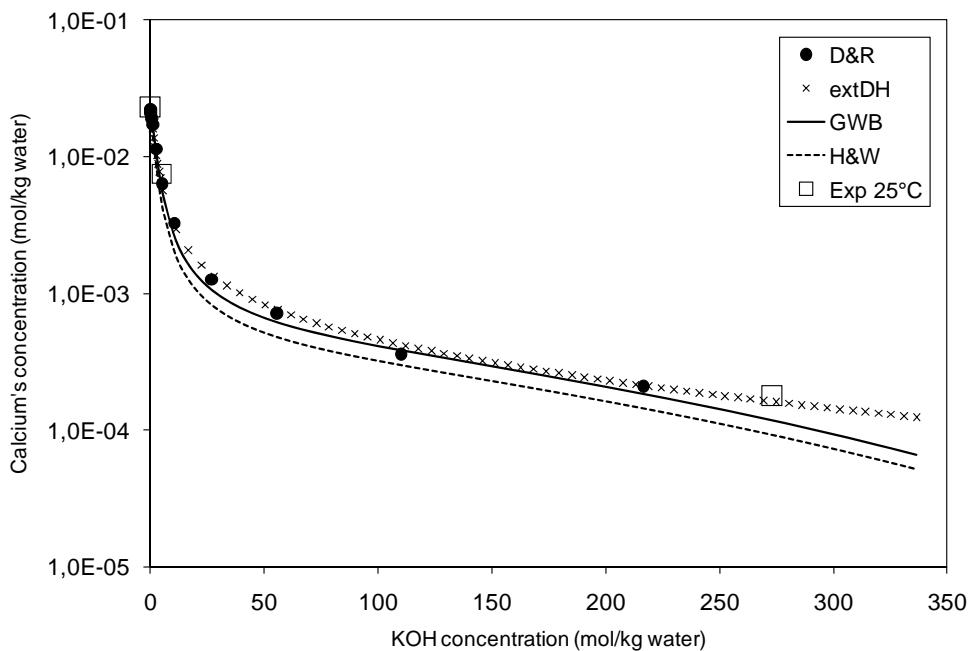
Albeit ICP-AES is very sensitive, Ca analysis is difficult in KOH solutions, because portlandite solubility is low and a matrix effect of potassium weakens the Ca signal, so that its calibration must be performed using KOH solutions rather than conventional (dilute) standards. This problem was overcome by using the standard addition method where the calibrating solutions are prepared at the same KOH concentration as the unknown samples and spiked with increasing amounts of calcium. This method enables the absolute calcium variations to be calibrated and the calcium present as impurities in the KOH parent solution (and thus in the standards) to be evaluated by regression.

According to [1], the carbonate solute content increases strongly with increasing KOH concentrations at equilibrium with calcite. Despite its enhanced solubility, however,

calcite reacts slowly in KOH solutions to produce secondary portlandite, and although equilibrium with portlandite seems to be obtained quickly, much of our runs remained undersaturated with respect to solid carbonate.

Despite these difficulties, our values of calcium hydroxide solubility compare well with those found in the literature [2] and extend the range of KOH concentrations and the temperatures where these data can be used to constrain thermodynamic models.

We used the ARXIM code, developed at Ecole des Mines de Saint Etienne, to compare these experimental solubility data with aqueous speciation models (figure 1).



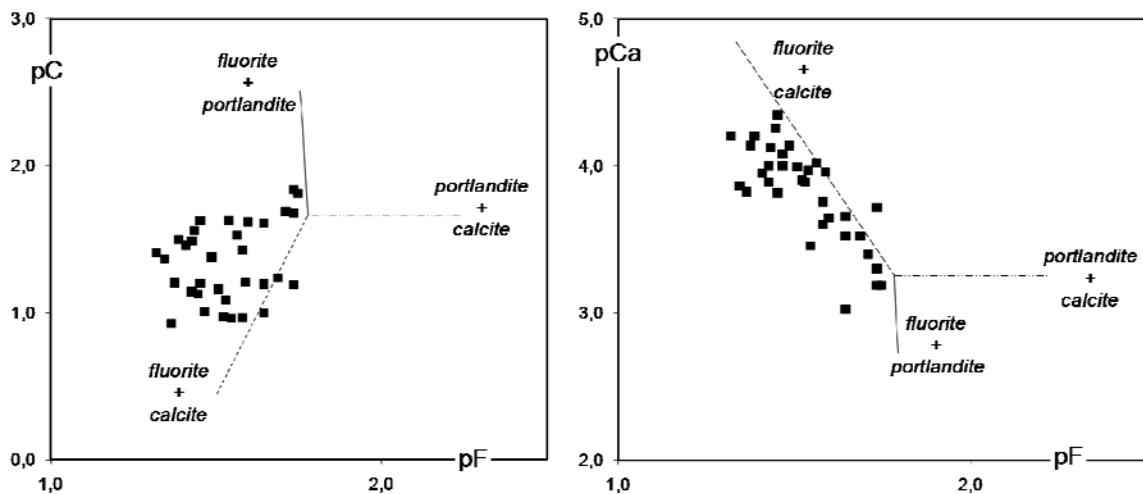
*Figure 1.* Calcium contents at equilibrium with portlandite in KOH solutions as predicted by extended Debye-Hückel (b-dot) model and various types of Pitzer's model parametrizations (GWB, H&W) at 25°C. Model equilibrium curves are compared with values obtained in the experiments (Exp 25°C) and those obtained by [2] (D&R).

Our experimental solubility values and those referenced in [1] for calcium compare well with those calculated with an extended Debye-Hückel (b-dot) and Pitzer type models. Quite unexpectedly, the extended Debye-Hückel model fits very well experimental data for calcium up to very high KOH concentrations. However, Pitzer-type models account much better for the carbonate enrichment in solutions equilibrated with both calcite and portlandite at high KOH concentrations.

To constrain the conditions of fluorite precipitation in the process, we need now to extend the speciation model to the system  $\text{Ca}(\text{OH})_2\text{-CaCO}_3\text{-CaF}_2\text{-KOH}\text{-H}_2\text{O}$ . Since a Pitzer model describes better the system's behaviour, we need to determine new Pitzer's interaction parameters in the range 15-35°C. Many of the required parameters are already documented at 25°C [2, 3, 4, 5], but fewer interaction data are documented as a function of temperature [6, 7, 8, 9, 10]. Thus, experiments are needed in order to

determine the parameters for the interactions  $\text{Ca}^{2+}/\text{F}^-$ ,  $\text{Ca}^{2+}/\text{CO}_3^{2-}$  and for  $\text{F}^-\text{-OH}^-$ . As first approximation we will consider that parameters for triple and ionic interactions of the same sign are negligible.

Mineral equilibria in this system will be explored by mixing KOH-KF solutions with suspensions of portlandite and/or calcite in KOH solutions. The guess is to locate the four phase equilibrium point (portlandite-calcite-fluorite-solution) as a function of KOH concentration and temperature. Of particular interest is the location of the portlandite-absent univariant line, which may exert a major control on process solutions (figure 2).



**Figure 2.** Hypothetical phase relationships for the system portlandite-calcite-fluorite in KOH solutions of fixed concentration. Solution compositions for Ca, F and C are reported as P-values ( $P = -\log C$ ) at equilibrium with solids and compared with test process data (squares).

Possible scenarios for fluorite precipitation and their kinetic limitations will ultimately rely on the assessment of over and undersaturations of the process solutions with respect to the three minerals.

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