

Experimental investigation of the stability of neodymium chloride complexes to 300°C

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Introduction

Until recently, it was widely believed that the Rare Earth Elements (*REE*) behave as immobile components during fluid-rock interaction. However, a growing body of field and theoretical evidence suggests that this is not always the case, and that hydrothermal processes, in particular, may be responsible for concentrating the *REE* to economically-exploitable levels. To better understand these processes, high temperature experimental data for aqueous compounds of the *REE* are desperately needed. In this study, the stabilities of the neodymium (Nd) chloride complexes are being determined in the temperature range 25 to 300°C.

Methods

The experiments of this study are based on a modification of the technique first used by Ruaya and Seward (1986). The solubility of AgCl is measured in solutions containing constant chloride molality, but varying ΣNd molality. Formation of Nd-chloride complexes changes the Cl mass balance to an extent which is proportional to their average ligand number. Because the solubility of AgCl is a sensitive indicator of any such change, the stoichiometry of the Nd chloride complexes can be obtained by varying $\Sigma\text{Cl}/\Sigma\text{Nd}$ in a series of parallel experiments.

Two sets of stock solutions containing 0.01, 0.03, 0.10, 0.30, 1.0, 3.0 and 5.0m ΣCl were prepared using either HCl/NaCl mixtures (1:10 mole ratio) or pure HCl. Each stock solution was split into 8 fractions, to which varying amounts of a highly soluble neodymium compound was added. For the pure HCl solutions, Nd was added in the form of $\text{Nd}_2\text{O}_3(\text{s})$; for the mixed solutions, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ was used. The solutions, along with small pellets of $\text{AgCl}(\text{s})$, were transferred to silica tubes which were sealed and placed inside simple pressure vessels. Temperature

was controlled using an electrical resistance furnace. Up to sixteen 9mm OD tubes were reacted simultaneously in the same pressure vessel. Run durations of 7–10 days were used (this was considered ample time to attain equilibrium at 200°C, based on the earlier results of Ruaya and Seward, 1986). At the end of the experiment, the pressure vessels were inverted, allowing separation of saturated solution from the AgCl pellets, which remained lodged at a narrow constriction in the tubes. The silver solubilities were then measured two ways: (1) mass loss of the AgCl pellets; and (2) digestion of fresh AgCl precipitate formed during the quench with NH_4OH , followed by AAS analysis.

Results

Approximately 100 silica tube experiments have been performed to date, covering the complete range of chloride concentrations at 200°C using either $\text{Nd}_2\text{O}_3\text{-HCl}$ or $\text{NdCl}_3\text{-NaCl-HCl}$ solutions (in some cases, both). A few runs have also been conducted at 300° and 21°C.

Figs. 1 and 2 summarize two sets of data, both collected at 200°C and 0.1m ΣCl . The data of Fig. 1 were collected using a Nd-oxide source and pure HCl solutions, whereas Nd-chloride and mixed HCl/NaCl solutions were used in Fig. 2. The experimental data (solid squares) show either a steady decrease (Fig. 1) or increase (Fig. 2) in AgCl solubility with increase in ΣNd molality. The lines labelled 0 to 4 show the change in AgCl solubility which is predicted, assuming that neodymium exists in solution as each one of the species NdCl_x^{3-x-} , where $x = 0$ to 4. The difference in topology of the 'forward modeling' curves between Figs. 1 and 2 is due to the effect of adding Nd as an oxide vs. a chloride salt on the ΣCl mass balance. Two important observations may be made: (1) the average ligand number of the Nd-chloride complexes is roughly 0.6–0.8; and (2) similar ligand numbers are obtained irrespective of

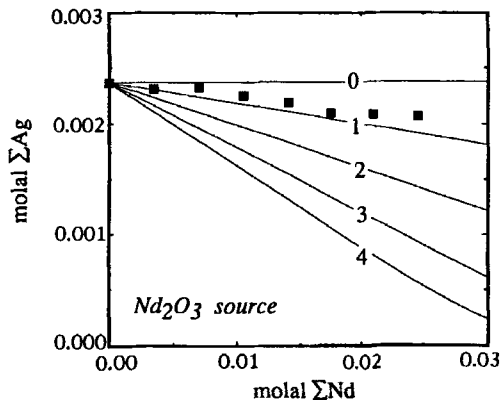


FIG. 1. AgCl solubility data at 200°C and 0.1m ΣCl , using $\text{Nd}_2\text{O}_3(\text{s})$ source (see text).

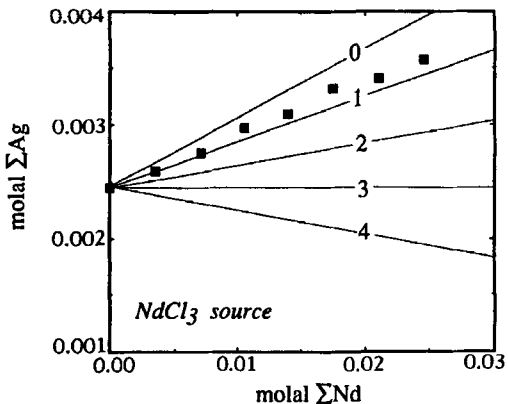


FIG. 2. AgCl solubility data at 200°C and 0.1m ΣCl , using $\text{NdCl}_3(\text{s})$ source (see text).

the form in which Nd is added. The second observation is strong evidence for the validity of our experimental method and forward modeling calculations.

Results at 0.03 and 0.10m ΣCl indicate a log K value of approximately $+2 \pm 0.5$ for the reaction: $\text{Nd}^{3+} + \text{Cl}^- = \text{NdCl}^{2+}$. This figure is somewhat higher than the theoretical prediction of Wood (1990). However, the present estimate is very preliminary, and may change once all of the data at 200°C are collected and interpreted by least squares regression. Other experiments at 200°C and higher ΣCl molalities (0.3 to 5.0) all indicate average ligand numbers close to unity, suggesting a very wide field of predominance for the simple NdCl^{2+} ion pair at 200°C. Results at 300°C and 1.0m ΣCl also indicate that NdCl^{2+} is dominant.

Conclusions and further work

Our solubility results show that the simple NdCl^{2+} ion pair will dominate over Nd^{3+} in hydrothermal solutions of moderate temperature (200° to 300°C) over a wide range of chloride concentrations (0.1 to 5.0m). Furthermore, the

evidence suggests that Nd-chloride complexes of higher ligand number are weak or non-existent at $T \leq 300^\circ\text{C}$. Experiments are in progress to extend our data base to higher and lower temperatures. We also plan to use the same experimental technique to investigate the stability of other REE-chloride complexes up to 350°C.

Although we have demonstrated that NdCl^{2+} is stable relative to the simple Nd^{3+} ion in high temperature fluids, it remains to be shown whether this complex (and analogous species for other REE) will dominate in solutions which contain elevated concentrations of competing ligands such as F^- , SO_4^{2-} and/or CO_3^{2-} . For example, Wood (1990) has predicted that fluoride complexes will control europium mobility in many hydrothermal brines, even at $a_{\text{Cl}^-}/a_{\text{F}^-}$ ratios $> 100,000$. Clearly, more experiments are needed on the aqueous behavior of this important group of metals.

References

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