The experimental investigation of the neodymium speciation in the water vapor

N.R. Zagrtdenov¹, A.Y. Bychkov¹,², I.Y. Nikolaeva¹
¹M.V. Lomonosov Moscow State University, Department of Geology, Moscow
²V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, Moscow

Abstract. New experimental data on the speciation of neodymium in the water vapor under hydrothermal conditions are presented.

Key words: hydrothermal process, speciation of rare earth elements, neodymium, water vapor.


Neodymium is usually associated with elements with low volatility, since its oxide has low fugacity in vacuum [Kazenans, Chizhikov, 1976]. However influence of other components such as water, chlorine or fluorine can increase the amount of matter which can be transported by gas. This effect has been noticed in such low-volatile elements as gallium, silver, gold, copper and others [Pokrovski et al., 2013]. These days there are evidences of the gaseous transport of rare earth elements (REE) under hydrothermal conditions. According to the article [Gilbert, Williams-Jones, 2008], there are data of encrustations enriched by REE from actively degassing fumaroles of natrocarbonatite volcano Oldoinyo Lengai, Tanzania, which were products of dissipation from volcanic gases. In addition, concentrations of REE and yttrium were analyzed in high enthalpy fluid of Larderello-Travale geothermal field, Tuscany (Central Italy) [Möller et al., 2003], where the abundance of REE range from 0.1 to 10 pmol/kg, also distribution factors between HEF and source rocks were defined.

Two methods have been used to study the solubility in the gaseous phase of Nd(OH)₃ and Nd₂O₃ statically in autoclaves and dynamically by the flow method. Analyze of literature showed that for combination of lanthanides and water both oxide Ln₂O₃ and hydroxides LnOOH, Ln(OH)₃ can be stable [Viswanathiah et al., 1980, Shafer, Roy, 1959]. In case of neodymium under conditions of our experiments hydroxide Nd(OH)₃ is not stable. Synthesis of stable phase was conducted according to the methods, stated in following articles: [Kutty et al., 1978; Viswanathiah et al., 1980]. Oxide Nd₂O₃ with stamp HO-E (OCT 48-197-81) was the initial phase. For obtaining the hydroxide the oxide powder was placed into autoclave with previously calculated amount of distilled water without CO₂ and was maintained under 400 °C and pressure 1 kbar during 15 days. Resulting phase was analyzed by X-ray powder diffraction, which confirmed that it is neodymium hydroxide Nd(OH)₃.

Experiments of neodymium transportation have been conducted through the use of static method in autoclaves under 200, 250 °C and pressure ranges from 3 to 15 and from 5 to 38 bar respectively (without reaching the saturation of the water vapor). The preparing of the experiment included volume calibration and lining of the autoclaves, calibration of the oven and preliminary calculations.

Before the experiment the definite amount of double distilled water was poured, this water set the pressure, which created only gaseous phase without liquid under experiment conditions. The pressure and density of saturated water vapor was taken from [Naumov et al., 1971]. Then the open titanium vial on the holder with the neodymium hydroxide was placed into the autoclave.

Autoclaves was maintained in the air thermostat SNOL-3.5 with fluctuation of the temperature ±1°C. The temperature was controlled by chromel – alumel thermocouple, duration of the experiments was 7 days.

During the experiment the water evaporated and the vapor interacted with solid phase in the vial. Components transported in the gaseous phase precipitated on the bottom and wall of the autoclave after the quenching (30-40 min in the reservoir with cold running water). After these operations the autoclave was opened and the vial with the neodymium hydroxide was retrieved. Washings were performed with a 10 ml of 3% solution HNO₃ under 200 °C to determine the amount of transferred material. Then autoclaves washing was repeated to determine the completeness of the operation.
The flow method has been used for exploration of Nd$_2$O$_3$ solubility in water vapor under 300, 350, 450°C and pressure ranges from 0.025 to 0.7 bar. The air flow, which speed was measured, passed through the two bubblers (with NaOH and water), which were placed in thermostat. There was the removal of carbon dioxide in the first bubble and the saturation of the water vapor under thermostat temperature in the second one. Thus the air flow of certain humidity has been forced through the quartz tube in the oven with Nd$_2$O$_3$ (stable phase under these conditions) under the operating temperature 300, 350 or 450°C, where there was a reaction of the solubility of the neodymium in the gaseous phase. The glass filter at the tube end delayed aerosol particles of neodymium oxide. As a result, the gas saturated with species, which can migrate in the vapor passed through the 3% solution of HNO$_3$, and the neodymium was trapped.

The solutions, which had been obtained by both methods were analyzed by ICP-MS (ELEMENT 2, Thermo Finnigan). The background solution was HNO$_3$ with concentration 3%. Indium with concentration 10 mcg/kg was added to the samples to control the intensity of sample supply. Solutions for calibration was prepared from standart solution for 69 elements of «Merk» company by serial dilution. ICP-MS data were calculated to the concentrations using methods, which were developed in Laboratory of the experimental geochemistry in Lomonosov Moscow State University.

The results of static experiments in the autoclaves demonstrated that the solubility of Nd(OH)$_3$ in water vapor doesn’t depend on the water pressure, hence the proposed reaction is as follows:

$$\text{Nd(OH)}_3^{(\text{solid})} = \text{Nd(OH)}_3^{(\text{gas})}\,.$$  

The logarithms of the equilibrium constants are 9.15±0.42 for 200 °C and -9.30±0.31 for 250°C.

In case of dynamic flow system experiments the solubility of Nd$_2$O$_3$ increases with water fugacity rising at all temperatures and the slope approximates 1.5. Thus, there can be assumed following reaction:

$$0.5 \text{Nd}_2\text{O}_3^{(\text{solid})} + 1.5 \text{H}_2\text{O}^{(\text{gas})} = \text{Nd(OH)}_3^{(\text{gas})}.$$  

The logarithms of the equilibrium constants for the reaction are 8.31±0.42 for 300 °C, -7.74±0.31 for 350 °C and -7.03±0.61 for 400 °C.

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References


