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E-pO^{2-} diagram for rare earth elements in molten salt

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Abstract: Electro-reduction of spent nuclear oxide fuels in molten salt was the key step of pyroprocessing for oxide fuel treatment. In the present study, the E-pO^{2-} diagram for rare earth elements in molten LiCl-KCl at 450 ºC were developed based available experimental data. E-pO^{2-} diagrams could show the stability of each chemical compound in the salt, and therefore, the diagrams could be applied to predict experimental conditions for electro-reduction of spent nuclear fuel efficiently. Compared with the available E-pO^{2-} diagrams, the present study concerned the activity coefficient of the element studied in the molten salt in all reactions, which made the diagram be more reliable and accurate.

Keywords: E-pO^{2-} Diagram; molten salt; pyroprocessing; fuel cycle; rare earths

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A pyrochemical processing system can process nuclear fuels with only a short cooling time after discharged from a reactor, and it can be collocated with a nuclear power plant[1]. Therefore, the need for off-site transportation of used nuclear fuel can be eliminated, which reduces proliferation concerns, risk of traffic accidents during transportation, and improves the economics for reprocessing. Pyrochemical test facilities have been deployed in U.S. and in several foreign countries, including Japan, China, India, Korea and European countries. The technology was, however, originally developed for processing the spent metallic fuels from EBR-II reactors in the U.S. and cannot be directly applied to the processing of used oxide fuels from commercial light-water-cooled reactors (LWRs). To utilize the technology for spent oxide fuels from LWRs, all the current pyroprocessing concepts need to be modified by adding a process[2] to reduce the oxide fuel to its metallic form before the electrorefining stage where the actinides are separated from the fission products. The reduction processes would introduce Li_2O[2,3] to the molten salt. Therefore, E-pO^{2-} diagrams of actinides and fission products (mainly rare earth (RE) metals) are needed to understand the experimental results and behaviors of RE metals during oxide fuel reduction, determine the oxide fuel reduction operation conditions, and develop reduction facilities.

In addition to the oxide fuel reduction, molten salt recycle is another key technology to enable a sustainable pyroprocessing and to yield a minimum amount of process waste[4]. During molten salt recycle, actinide and rare earth metal drawdown processes are the key steps in which actinides and rare earth metals are separated from the molten salt, respectively. Therefore, the E-pO^{2-} diagrams which can show the stable phases of actinide and rare earth in the molten salt as a function of oxygen potential are also very important for the drawdown processes, especially for cases when the molten salt is contaminated by ingression of moisture or air.

The electrochemical behaviors for rare earth elements and rare earth alloy in molten salt have been studied for years (e.g.[5,6]).There have been many E-pO^{2-} diagram for some common rare earth elements (La, Nd) (e.g.[3]) in molten salt and also there have been some studies about E-pO^{2-} diagrams for actinides (U, Np, Pu) (e.g.[7,8]). Most of the thermodynamic data of rare earth metals in molten KCl-LiCl have been recently reported[9], which make it possible to develop the E-pO^{2-} diagrams of rare earth metals in molten KCl-LiCl. The present study deduced the E-pO^{2-} diagrams of the rare metals for which the necessary thermodynamic data were available. Compared with previous studies, the present study systemically reported the E-pO^{2-} diagrams of most of the rare earth metals in molten KCl-LiCl, which make it easy to make comparisons between different metals. Furthermore, the present study concerned the activity coefficient of the RE ions in the salt which made the diagram more accurate compared with previous studies, most of which assumed the activity coefficient to be 1.

1 Thermodynamic data

The apparent potential of the RE^{3+}/RE^0 was determined from an electrochemical process, which can be shown in a reaction as:

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$$RE^{n+}+ne^{-}=RE \quad (1)$$

When the reaction is in equilibrium, the relationship between equilibrium potential and standard potential follows the Nernst equation; the Nernst equation is used to describe the reduction potential of a cell under non-standard condition.

$$E_{\text{reduction}} = E^{0}_{\text{reduction}} + \frac{2.3RT}{nF}\lg\left(\frac{\alpha_{\text{oxidation}}}{\alpha_{\text{reduction}}}\right) \quad (2)$$

where $E_{\text{reduction}}$ is the reduction equilibrium potential, $E^{0}_{\text{reduction}}$ is the standard reduction potential, R is the gas constant, T is the temperature, n is the number of moles of electrons transferred during the reaction, F is the Faraday constant, and a is the chemical activity for the specific species, $\alpha_{\text{reduction}}$ is the activity of oxidizing agent and $\alpha_{\text{reduction}}$ is the activity of reducing agent.

Based on the existed Nernst equation and considering that the activity of the reduction metal is 1, the equilibrium potential reaction between rare earth elements can be modified to the equation as the following equation.

$$E_{\text{RE}^{n+}/\text{RE}^{0}} = E^{0}_{\text{RE}^{n+}/\text{RE}^{0}} + \frac{2.3RT}{nF}\lg\gamma_{\text{RECl}_n}X_{\text{RECl}_n} \quad (3)$$

where $E_{\text{RE}^{n+}/\text{RE}^{0}}$ is the equilibrium potential of reaction and $E^{0}_{\text{RE}^{n+}/\text{RE}^{0}}$ is the standard potential which is calculated from the changing of Gibbs free energy of formation to the reaction between the pure compounds. X_{RECl_n} represents mole fraction of the oxidizing agent. In the equation, RECl_n represents all the form of chloride salt for the entire rare earth elements.

The apparent potential is defined by:

$$E^{\text{ap}}_{\text{RE}^{n+}/\text{RE}^{0}} = E^{0}_{\text{RE}^{n+}/\text{RE}^{0}} + \frac{2.3RT}{nF}\lg\gamma_{\text{RECl}_n} \quad (4)$$

Then the equilibrium potential can be expressed using apparent potential:

$$E_{\text{RE}^{n+}/\text{RE}^{0}} = E^{\text{ap}}_{\text{RE}^{n+}/\text{RE}^{0}} + \frac{2.3RT}{nF}\lg\gamma_{\text{RECl}_n} \quad (5)$$

and the activity coefficient can also be calculated based on Eq. (3) and the relationship between the standard potential and the Gibbs free energy of formation:

$$\lg\gamma_{\text{RECl}_3} = \frac{n*F*E^{\text{ap}}_{\text{RE}^{n+}/\text{RE}^{0}} - \Delta G^{0}_{\text{RECl}_n}}{2.3RT} \quad (6)$$

where F is the Faraday constant (96485 J/mol), $\Delta G^{0}_{\text{RECl}_n}$ is the Gibbs free energy of formation of RECl_n, R is the gas constant and T is the temperature in kelvin. The apparent potential, the standard potential, and calculated activity coefficients based on available experimental data at 723 K are given in Table 1. The available apparent potentials were summarized in reference[9]. Comparisons were made between different measurements in the reference, therefore, in this paper, the recommended apparent potential and the activity coefficient given in the reference[9] were used directly. The activity coefficient gave an idea of the cationcomplexation in the molten salt. The rare earth element, which has a smaller activity coefficient, can form strong complexes with the chloride ion in the molten salt.

Table 1 Apparent potential, standard potential and activity coefficient of $ReCl_3$ at 723 K

	Formation of Gibss free energy	Standard potential E^0/V	$\lg\gamma_{\text{RECl}_3}$	Apparent potential E_{ap}/V
Ce (3+/0)	–874.940[10]	–3.023	–1.735[9]	–3.106[9]
Eu (3+/2+)	–748.281[10]	–2.585	–2.944[9]	–0.857[9]
Gd (3+/0)	–828.181[10]	–2.861	–2.579[9]	–2.984[9]
La (3+/0)	–873.002[10]	–3.016	–2.524[9]	–3.137[9]
Nd (3+/0)	–850.226[10]	–2.937	–3.681[9]	–3.113[9]
Pr (3+/0)	–861.680[10]	–2.977	–2.283[9]	–3.086[9]
Y (3+/0)	–820.979[10]	–2.836	–5.638[9]	–3.106[9]
Sm (3+/2+)	–846.016[10]	–2.923	–4.350[9]	–2.060[9]
Yb (3+/2+)	–784.734[10]	–2.711	–2.205[7]	–1.660[11]
Tb (3+/0)	–817.130[10]	–2.823	–4.503[8]	–3.038[12]
Er (3+/0)	–814.286[10]	–2.813	–5.587[9]	–3.080[13]
Ho (3+/0)	–824.665[10]	–2.849	–2.889[10]	–2.987[14]
Sc (3+/0)	–753.904[10]	–2.605	–5.170[11]	–2.851[15]

2 *E*-*p*O2 diagram development

2.1 Determination of solubility products

Several oxide compounds of rare earth metals can be formed by oxidation states (III) and (IV). The compounds that have formation of REOCl, RE_2O_3 and REO_2 are usually considered in developing the diagram. According to Mottot[16], the solubility product can be determined using the expression:

$$pK_s(RE_2O_3)=\lg K_1^{*}-6\lg\alpha_{\text{LiCl}}+2\lg\gamma_{\text{RECl}_3}+3\lg\gamma_{\text{Li}_2\text{O}} \quad (7)$$

The value of K_1^{*} is the equilibrium constant for the related reaction between pure compounds. K_s is the equilibrium constant for the dissolution of an ionic compound during the reaction. pK_s means the $-\lg_{10}K$. This value can be calculated from the thermo chemical data from the reference[10] based on the following reaction:

$$RE_2O_3+6LiCl \xleftrightarrow{K_1^{*}} 2RECl_3+3Li_2O \quad (8)$$

Furthermore, it is also possible to calculate the solubility product of REOCl based on the expression:

$$pK_s(REOCl)=\lg K_2^{*}-2\lg\alpha_{\text{LiCl}}+\lg\gamma_{\text{RECl}_3}+\lg\gamma_{\text{Li}_2\text{O}} \quad (9)$$

where K_2^{*} is the equilibrium constant corresponding to the reactions:

$$REOCl+2LiCl \xleftrightarrow{K_2^{*}} RECl_3+Li_2O \quad (10)$$

where α_{LiCl} is the activity of the LiCl in the melt, which was obtained from the literature, and it is equal to 0.364[17] at 723 K. $\gamma_{\text{Li}_2\text{O}}$ is the activity coefficient of Li_2O and $\gamma_{\text{Li}_2\text{O}}=10^{-5.2}$ at 723 K according to Séon[17].

2.2 *E*-*p*O^{2-} diagram development

The *E*-*p*O^{2-} diagrams of rare earth in molten LiCl-KCl