Study of Potentiometry for Monitoring Activity of GdCl$_3$ in Molten LiCl-KCl Salt

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In pyroprocessing spent nuclear fuels by electrorefining in molten LiCl-KCl salt, it is desired to monitor in real time the UCl$_3$ concentration in the salt for safeguards purposes. Current chemical analysis of the highly radioactive salt for electrorefining by an inductively coupled plasma technique is inconvenient and usually time-consuming in generating the salt composition results. In this paper, we evaluated whether a simple potentiometry approach can be used for real-time monitoring the concentration of GdCl$_3$, which was used as a surrogate for UCl$_3$, in LiCl-KCl-GdCl$_3$ salt by measuring the open circuit potential of a Gd metal electrode with respect to a Ag/AgCl reference electrode (RE) when GdCl$_3$ salt was incrementally added to the LiCl-KCl salt. Additions of LaCl$_3$, CeCl$_3$, and NdCl$_3$ salts were used for evaluating the effects of other chloride salts on the selectivity of the Gd metal electrode vs Ag/AgCl RE. While using potentiometry to determine GdCl$_3$ concentrations, Gd metal was unexpectedly observed to be unstable and dissolved in LiCl-KCl salt when GdCl$_3$ is present.

Some flowsheets for pyroprocessing of spent oxide fuels (based on UO$_2$ or UO$_2$/PuO$_2$ compositions) involve two electrochemical operations: oxide reduction and uranium electrorefining. During oxide reduction, oxide fuel is electrochemically reduced to metal. This typically involves a LiCl salt with 1 wt% Li$_2$O at 650 °C; the oxide fuel is reduced to metal at a cathodic electrode and oxygen gas is liberated from the molten salt at an anodic electrode. During uranium electrorefining, purified uranium metal is electrochemically recovered from the metal produced during oxide reduction. This usually involves a LiCl-KCl eutectic salt with about 6 wt% UCl$_3$ at 500 °C; the reduced metal is oxidized at an anodic electrode and electrorefined uranium metal is recovered at a cathodic electrode. Metals that are more reactive than uranium accumulate in the molten salt as metal chlorides. For safeguards purposes, it is necessary to know the concentrations of metals in the salt, particularly the concentrations of UCl$_3$, PuCl$_3$ and other actinide chlorides.

The composition of the LiCl-KCl salt for electrorefining can be analyzed by using techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES),$^{3,4}$ inductively coupled plasma mass spectrometry (ICP-MS),$^{5}$ and thermal ionization mass spectrometry.$^{6}$ However, because the electrorefining operations are conducted in hot cells, and because electrorefiner salts are highly radioactive, analytical results by these means are inconvenient to obtain. Special facilities and equipment are required just to collect the salt samples and transfer them to the analytical laboratory, where they are digested and diluted prior to undergoing analysis by the instruments. This is typically a very expensive, time-consuming process. Nevertheless, it is the most common means of analyzing radioactive salt samples at many institutions, including Idaho National Laboratory (INL) which has the country’s only pyroprocessing facilities for used nuclear fuels.

Potentiometry is a well-established method for analyzing both aqueous and molten salt electrolytes.$^{7–10}$ It is based on the measurement of open circuit potentials (OCPs), also known as electromotive force (EMF) potentials, of an electrochemical cell. The OCP is dependent on temperature and the chemical activities of the species involved in the two half-cell reactions that comprise the overall cell reaction. Typical potentiometry measurements use a reference electrode (RE) and a working electrode (WE) to complete the electrochemical cell. For example, the common EMF series in aqueous electrochemistry is based on OCP measurements of various half-cell reactions (under standardized conditions of temperature and concentration) relative to a standard hydrogen electrode. In simple electrochemical systems, in which the half-cell reactions at the reference and working electrodes are thermodynamically fully characterized, the OCP measurement can be used to determine the activity of electroactive species at the working electrode. A pH meter for measuring hydrogen ion activity in water is one such example.$^{11,12}$

A potentiometry approach is seldom used for chemical analysis in molten salt systems, probably due to the fact that molten salt systems are complicated and a good working electrode that selectively responds to the component to be tested is difficult to find. Recently, Bagri and Simpson$^7$ studied the activity of GdCl$_3$ in LiCl-KCl salts and the effect of CsCl on the activity of GdCl$_3$, using a GdCl$_3$ solute reference electrode and reported the activity coefficient of GdCl$_3$ compared to literature data. Their results showed that at the GdCl$_3$ concentration range of 0.4 to 1.5 mol%, the activity coefficient of GdCl$_3$ appeared reasonably constant; at a higher GdCl$_3$ concentration range, the activity coefficient increased with GdCl$_3$ concentration. However, it is unknown from their study how other elements besides Cs would affect the OCP measurements. It is possible that some elements may affect the potential of a Gd metal electrode, while other elements may not.

In the LiCl-KCl salt used for electrorefining spent nuclear fuels, the concentration of UCl$_3$ is usually around 6 wt% (or 0.01 molar fraction). We hypothesize that if the activity coefficient of UCl$_3$ is constant at a relevant range that covers 6 wt% and if the activity coefficient is not significantly affected by other chloride salt components such as NdCl$_3$, CeCl$_3$, and LaCl$_3$ in the molten LiCl-KCl salt, it is possible to use a potentiometry method to measure the UCl$_3$ concentration and, thereby, detect any significant deviation of the normal salt composition during electrorefining. To test the hypothesis, some surrogate work was initially proposed to verify the feasibility of this method.

In this study, we report on the feasibility of a potentiometry approach—using GdCl$_3$ and Gd metal as surrogates for UCl$_3$ and U metal respectively—for monitoring the GdCl$_3$ concentration in LiCl-KCl salt and determining the activity coefficient of GdCl$_3$. We also evaluate whether the presence of NdCl$_3$, CeCl$_3$ and LaCl$_3$, the three main salt components in the salt for electrorefining, would affect the activity of GdCl$_3$. Additional phenomena observed during the experimental potentiometry study are also reported.

**Experimental**

**Chemicals.**—The chemicals used in the experiments were as follows. LiCl–KCl eutectic salt and GdCl$_3$ salt (99.99 wt% pure)
were ultra-dry, contained in glass ampules. CeCl₃, LaCl₃ and NdCl₃ salt were anhydrous and all with 99.9 wt% purity. (Usually, anhydrous salts have a relatively higher moisture content but are less expensive than ultra-dry salts contained in glass ampules.) LiCl–KCl–I wt% AgCl salt and 99.99% Ag wire were used for fabricating a Ag/AgCl RE, and 99.99% Gd metal foil, 1 mm × 25 mm × 25 mm, was used as a working electrode. All chemicals were purchased from Alfa Aesar, except the Gd metal foil, which was purchased from Sigma Aldrich.

**Experimental procedures.**—The experimental setup for the potentiometry measurements is schematically shown in Fig. 1. A 1-mm diameter Ag wire inserted in LiCl–KCl–I wt% AgCl salt contained in a mullite closed end tube (5 mm inside diameter and 1 mm wall thickness) was used as a Ag/AgCl RE. The top of the mullite tube was sealed with epoxy.

203 g of LiCl–KCl eutectic salt was added to an alumina crucible of 93 mm inside diameter, and then the crucible was loaded into a furnace housed in a glovebox filled with argon gas. After the Ag/AgCl RE was inserted into the salt powder, the crucible was heated to about 769 K and maintained at that temperature for more than 15 h to ensure that the Ag/AgCl RE is in full equilibrium with the molten salt.

To make the Gd metal electrode, a small piece of Gd foil (1 mm thick) was first cut, in the glovebox, using scissors and then clamped using a stainless steel rod with a split end. The surface of the Gd metal foil was lightly filed so that the surface oxide (Gd is sensitive to air and moisture) was removed and a fresh Gd surface contacted the salt. Next, the Gd metal electrode was slowly inserted into the molten LiCl–KCl salt. As shown in Fig. 1, only the Gd metal part was immersed in the molten salt.

The OCP between the Gd metal electrode and the Ag/AgCl RE was measured and recorded by a Solartron 1287 potentiostat with a sampling rate of once per second. After the OCP reading was stable or the system was in equilibrium, a small amount of GdCl₃ salt was added. During the potentiometry measurements, it was difficult to know, based on the OCP measurements, whether or when the system has reached equilibrium. Based on experimental experience, typically when the OCP change is less than 0.5 mV in two hrs, we considered the system has reached equilibrium. A stable OCP measurement is important because for GdCl₃ monitoring purposes, the concentration determined by potentiometry is dependent on the OCP value. Following the GdCl₃ salt addition and stable OCP reading, another GdCl₃ addition was made. This process continued until the sixth or final GdCl₃ concentration of ~0.014 molar fraction in the LiCl–KCl salt was reached. A final GdCl₃ concentration of ~0.014 molar fraction was selected in this study so that the molar fraction of GdCl₃ was slightly higher than the typical molar fraction of UCl₃ in the LiCl–KCl salt for electrorefining.

To evaluate the selectivity of a Gd metal electrode or how other typical salt components in the ER salt might affect the results of the potentiometry measurements, a stable OCP reading was achieved upon the potentiometry addition, after a stable OCP reading was achieved. An increase in the molar fraction of CeCl₃, LaCl₃ and NdCl₃ salt was 0.0014, 0.0028, and 0.010 respectively. In this study, 15 h to ensure that the Ag/AgCl RE is in full equilibrium with the molten salt.

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The slope 0.0488 in the equation is 96% of the calculated value at 769 K, the relationship between the OCP (V) and molar fraction of GdCl₃ (X_{GdCl₃}) can be expressed as

\[
OCP = (-1.795 \pm 0.002) + (0.0488 \pm 0.0006) \log X_{GdCl₃} \quad \text{[1]}
\]

The slope 0.0488 in the equation is 96% of the calculated value at the test temperature from the Nernst equation, given as

\[
\frac{RT}{3F} \ln 10 = 8.314 \times 769 \times \ln 10 = 0.0509, \text{ where } R \text{ is the gas}
\]
Figure 2. (a) Overall OCP measurement for Gd vs Ag/AgCl RE over time when GdCl₃ salt was incrementally added to the LiCl-KCl salt, at 769 K, the inset is a close-up look at the first 5 h that more clearly illustrates the change in OCP after the first and second GdCl₃ additions were made. (Note: due to limited access to the facility, no GdCl₃ salt was added between 54 h to 110 h, i.e. between the 5th and 6th GdCl₃ additions, despite an equilibrium having been reached). (b) A magnified figure with higher resolution of OCP vs time showing the OCP changes between the 5th and 6th GdCl₃ additions.
constant, T is the temperature in K, and F is the Faraday constant 96485 C/mol. This suggests that, for the tested GdCl₃ concentrations of 0.0005 to 0.014 molar fraction, the activity coefficient of GdCl₃ in the LiCl-KCl-GdCl₃ salt is constant; therefore, the potentiometry technique can be considered applicable for real-time monitoring of the GdCl₃ concentration of a ternary LiCl-KCl-GdCl₃ salt system and determination of the activity coefficient of GdCl₃, when no other chloride salts are present.

**Effects of LaCl₃, CeCl₃ and NdCl₃ on Selectivity.**—Figure 4a shows the OCP measurements vs time for when LaCl₃ and CeCl₃ salts were added into the LiCl-KCl-0.014 GdCl₃ (in molar fraction) salt, after the six incremental GdCl₃ addition. The OCP did not appear to change after LaCl₃ and CeCl₃ additions. Therefore, LaCl₃ and CeCl₃, in the tested amounts and LiCl-KCl-GdCl₃ composition, can be considered to have no impact on OCP measurements.

Unlike LaCl₃ and CeCl₃, after each NdCl₃ salt addition, the OCP increased immediately and then decreased over time and reached a stable value, about 2.5 mV higher than that before the NdCl₃ addition, as shown in Fig. 4b. After a total of four NdCl₃ additions were made, an OCP increase of 10 mV was observed. This shows that the presence of NdCl₃ can affect the potentiometry technique for real-time monitoring of LiCl-KCl-GdCl₃ salt.

The reason for the effect of NdCl₃ additions on OCP measurements is not completely understood. There are two possibilities: (1) the NdCl₃ increased the activity coefficient of GdCl₃ or (2) some chemical reaction between the Gd metal and NdCl₃ occurred, causing the formation of GdCl₂ and dissolved Nd metal.

A voltammetry study conducted by Misra et al. in LiCl-KCl-5 wt% LnCl₃ (Ce, Gd, La, and Nd etc.) salt system at 773 K found that the reduction potential (vs Ag/AgCl RE) for Nd³⁺/Nd and Gd³⁺/Gd couples is −1.88 V and −1.93 V respectively. The more positive reduction potential for Nd³⁺/Nd than for Gd³⁺/Gd suggests that the reaction 3NdCl₃ + Gd = GdCl₄ + 3NdCl₂ or NdCl₃ + Gd = GdCl₃ + Nd is possible. The reduction potential for La³⁺/La and Ce³⁺/Ce couples is −1.96 V and −2.11 V, respectively, both of which are more negative than that for Gd³⁺/Gd couple, suggesting the reaction between LaCl₃ or CeCl₃ with Gd is unlikely.

**Activity coefficient of GdCl₃ in LiCl-KCl-GdCl₃ salt system.**—For the purposes of monitoring the GdCl₃ concentrations, if we have a reliable calibration and the activity coefficient of GdCl₃ is constant in the LiCl-KCl-GdCl₃ salts, we can measure the GdCl₃ concentration based on the OCP measurement without knowing the activity coefficient, because the activity coefficient has already been included in the equation for concentration measurement, as shown in Eq. 1. But it is also useful to know the activity coefficient—an important thermodynamic parameter for molten salt chemistry—and compare this number with others’ data. If the activity coefficient of GdCl₃ determined by the OCP measurement method in this study is consistent with literature values that were calculated using other methods such as voltammetry or OCP measurement using similar reference electrodes, that means the potentiometry based on Gd vs Ag/AgCl RE for GdCl₃ concentration measurement is quite reliable. If it is inconsistent with established literature values, we need to understand the underlying reasons for the inconsistency, and the feasibility of potentiometry based on Gd vs Ag/AgCl RE for GdCl₃ concentration measurement may be questionable.

Because of the different experimental testing conditions and various standard states used in literature, the derived activity coefficients achieved differ drastically. Bagri and Simpson, in a recent study, summarized the reported activity coefficient of GdCl₃ salt in LiCl-KCl salts, and compared their results using a Gd metal electrode and a reference electrode with Gd metal in a GdCl₃-saturated LiCl-KCl salt.

To calculate the formal potential and activity coefficient of GdCl₃, its Gibbs free energy of formation must be known, and it is needed to convert the Gd metal electrode potential vs the Ag/AgCl RE to a potential vs the Cl₂/Cl⁻ RE. For convenience, the potential difference of Ag/AgCl RE with respect to a Cl₂/Cl⁻ electrode from a

![Figure 3. Plot of OCP (Gd vs Ag/AgCl RE) vs GdCl₃ molar fraction in the LiCl-KCl salt at 769 K.](image-url)
recent study by Yoon et al.\textsuperscript{15} was used here. At 773 K, the Ag/AgCl electrode vs Cl_2/Cl^− \text{RE} is –1.21 V.

Based on the thermodynamics of the electrochemical cell, Gd\text{LiCl-KCl-xGdCl}_3\text{mullite membrane}|\text{LiCl-KCl-1wt\%AgCl}|\text{Ag}, the half-cell electrochemical reactions (both in reduction forms) are as follows:

\[
\begin{align*}
\gamma^+ = \gamma^+ (\text{GdCl}_3^3\text{Cl}^3\text{Cl}) + \frac{RT}{F} \ln (\gamma_{\text{GdCl}_3}) X_{\text{GdCl}_3} & \quad [2] \\
\gamma^+ = \gamma^+ (\text{AgCl}) + \frac{RT}{F} \ln (\gamma_{\text{AgCl}}) X_{\text{AgCl}} & \quad [3]
\end{align*}
\]

where \(E^{eq}_{\text{Gd}}\) and \(E^{eq}_{\text{Ag}}\) are the equilibrium potential, \(E^{0}_{\text{GdCl}_3/\text{Gd}}\) and \(E^{0}_{\text{AgCl}}\) are standard electrode potential for Gd/GdCl_3 and Ag/AgCl couples, \(\gamma_{\text{GdCl}_3}\) and \(\gamma_{\text{AgCl}}\) are activity coefficients of GdCl_3 and AgCl, \(X_{\text{GdCl}_3}\) and \(X_{\text{AgCl}}\) are the molar fractions of GdCl_3 and AgCl, respectively.

The measured OCP, or \(E^{eq}\) as usually used in most literature, at equilibrium at test temperature \(T\) (K) can be expressed as the difference of \(E^{eq}_{\text{Gd}}\) and \(E^{eq}_{\text{Ag}}\):

\[
E^{eq} = E^{eq}_{\text{Gd}} - E^{eq}_{\text{Ag}} \quad [4]
\]

As mentioned above, for the specific LiCl-KCl-1wt\%AgCl salt in Ag/AgCl RE used in this study, the potential difference of \(E^{eq}_{\text{Ag}}\) and standard Cl_2/Cl^− electrode \(E^{0}_{\text{Cl}_2/\text{Cl}^-}\) is –1.21 at 773 K, which is very close to the measured salt temperature (769 K) in the present study. Using a standard Cl_2/Cl^− reference, with a potential of zero, the Eq. 4 can be simplified as:

Figure 4. OCP measurements when CeCl_3 and LaCl_3 salts (a) and NdCl_3 (b) salt were added to the LiCl-KCl-GdCl_3 salt at 769 K.
where \( E_{G_{\text{Cl}3/Gd}}^{0} \) is the standard reduction potential of GdCl₃. In molten salt electrochemistry, a pure salt at liquid state is normally used as the standard state. But because of test temperature at 769 K is below the melting point of GdCl₃, usually a hypothetical super-cooled liquid at the test temperature was used as standard state. Some literature was available on calculating the standard electrode potential for the Gd/GdCl₃ couple using super-cooled liquid state as standard state. For convenience, the calculated standard potential \( E_{G_{\text{Cl}3/Gd}}^{0} \) vs temperature—\( E_{G_{\text{Cl}3/Gd}}^{0} = -3.3478 + 7 \times 10^{-4}T \)— in a study by Bagri et al. was used here. At the test temperature (769 K) in this study, the standard potential of GdCl₃ is \(-2.810 \text{ V}\).

According to the experimental OCP data in this study, the calculated activity coefficient of GdCl₃ is \(1.7 \times 10^{-4}\) in the LiCl-KCl-GdCl₃ salt system, at the tested GdCl₃ concentrations of 0.0005 to 0.014 molar fraction. This activity coefficient based on OCP measurements is similar to the reported data of \(1.7 \times 10^{-4}\) for 2 wt% GdCl₃ at 773 K by Tang and Pesic and \(1.5 \times 10^{-4}\) for 0.17 mol% GdCl₃ at 771 K by Caravaca et al. with voltammetry technique and Ag/AgCl RE being used in both cases, but higher than that measured \((5.3 \times 10^{-5}\) for 1.5 wt% GdCl₃ at 773 K) by Bagri and Simpson, using saturated GdCl₃ salt in LiCl-KCl-GdCl₃ contained in a mullite tube as reference electrode. The comparison with typical literature data in terms of GdCl₃ activity coefficient in LiCl-KCl-GdCl₃ salt suggests that if the same or similar Ag/AgCl RE is used, the calculated GdCl₃ activity coefficient measured by multiple institutions is consistent and quite close. This may also suggest that potentiometry using Gd vs Ag/AgCl RE can be considered reliable.

**Stability of the Gd electrode in LiCl-KCl-GdCl₃ salt system.**— During the experiments, the Gd metal electrode was found to exhibit dissolution into the salt. Figure 5 shows a photograph of a Gd electrode used before and after the experiment, clearly showing that most of the Gd metal foil was gone. Although the initial weight of the Gd metal was used before and after the experiment, clearly showing that most of the dissolution into the salt. Figure 5 shows a photograph of a Gd electrode.

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Upon completion of experiments, a small amount of salt was transferred out of glovebox to a fume hood. When water was added into a beaker containing the salt, strong bubbling was observed. Likely due to the reaction between Gd with water, hydrogen gas was generated and result in the bubbling.

The disappearance of the Gd metal suggests that in a LiCl-KCl salt containing GdCl₃, the Gd metal may have some solubility in the salt. In other salt mixtures of a metal and a metal’s halide liquid, some solubilities of metal in the molten salts have been reported. For example, in an Oak Ridge National Laboratory report, Bredig listed some metal-metal halide phase diagrams, clearly showing the solubility of some metals in their metal halides. It has been known that Li metal has some solubility in LiCl-1wt% Li₂O salt, and Be has some solubility in LiF-BeF₂ salt.

Upon a close examination of the crucible after completing the experiments, and of unpublished behavior of metal uranium in LiCl-KCl-UCl₃ salt for electrorefining, the idea that Gd has some solubility in a LiCl-KCl-GdCl₃ salt system seems perhaps somewhat inaccurate. In the LiCl-KCl-GdCl₃ salt after potentiometry measurements, some black deposits were expected Gd metal deposits were observed at the bottom of the crucible crucible. For the LiCl-KCl-UCl₃ salt for uranium electrorefining, when uranium dendrites contained in a stainless steel anode basket were in contact with LiCl-KCl-UCl₃ salt at 500 °C for quite a long time (about one month or longer), the uranium dendrites had disappeared; however, some uranium dendrites were found at the bottom of the crucible containing the LiCl-KCl-UCl₃ salt. The underlying reason behind the Gd dissolution in LiCl-KCl-GdCl₃ salt remains unknown; however additional testing is being performed. One possible explanation is that the exchange current might be high. When the Gd metal contacts liquid LiCl-KCl-GdCl₃ salt, an equilibrium between Gd and GdCl₃ in the salt exists: Gd(metal) ‖ Gd³⁺(salt). Ideally, when the exchange current is low, the Gd³⁺ ions formed from the Gd metal dissolution would deposit back onto the Gd metal, thus forming an equilibrium. But when the Gd exchange current is high, some Gd³⁺ ions, instead of depositing back to the Gd metal surface, diffused into the salt and slowly sank at the bottom of the crucible, continuing the dissolution of Gd.

ICP-MS is typically used for analyzing the salt compositions. Upon the completion of the experiments, a salt sample was analyzed by ICP-MS and the result was shown in Table I. The concentration (in molar fraction) of LaCl₃, CeCl₃ and NdCl₃, measured by ICP-MS is consistent with the calculated values based on the mass of the salts added during experiments. However, the GdCl₃ molar fraction by ICP-MS is 14.2% greater than the calculated value based on salts added in experiments, because of the presence of the dissolved Gd metal in the salt. Given that an estimated 1.5 g of Gd metal electrode was dissolved in the salt, the expected GdCl₃ molar fraction—which includes the contribution from the dissolved Gd metal—measured by ICP-MS should be 0.016, which is close to the actual value (0.0155) measured by ICP-MS measurement. This suggests that ICP-MS is reliable for determining the total Gd concentration in the salt. However, we were more interested in knowing the GdCl₃...
concentration, not the total Gd. In the LiCl-KCl-GdCl₃ salt in this study, both GdCl₃ and dissolved Gd metal were present. When a salt sample was analyzed by ICP-MS, the Gd metal (or Gd⁶⁺) was first converted to Gd⁴⁺ during the sample preparation, and the final GdCl₃ concentration determined by ICP-MS would be greater than the true GdCl₃ concentration. To achieve an accurate analysis of the GdCl₃ concentration in the salt, the contribution of dissolved Gd metal needs to be removed.

Because of the significantly higher GdCl₃ concentration measured by ICP-MS when dissolved Gd metal is present in the salt, ICP-MS cannot be used as a reliable technique for monitoring purposes. This is the same for the uranium electrorefining because the uranium metal was found to be dissolved in LiCl-KCl-UCl₃ salt for electrorefining. This is also why the potentiometry herein was proposed for monitoring GdCl₃ or UCl₃ in molten salt and removing the effects from dissolved Gd or U metal. It is worth noting that though some rare earth metals like La, Ce, Pr, and Nd were found to be dissolved in the rare earth halides (chloride, bromide, and iodide), the phenomenon of uranium metal being dissolved in LiCl-KCl-UCl₃ salt was not reported in literature, and we just found this phenomenon in recent years.

Further Discussion on Potentiometry for Monitoring Uranium Electrorefining Operation

In the potentiometry measurement in this study, the OCP between the Gd/GdCl₃ in equilibrium and Ag/AgCl RE is the basis for GdCl₃ concentration monitoring. Any factors that affect either Gd/GdCl₃ equilibrium potential and the Ag/AgCl RE could lead to OCP changes. Generally, based on our experience, the potential of Ag/AgCl RE is quite stable in LiCl-KCl salt system for long term (e.g. 4 to 5 weeks) operation. But some small variations (e.g. about 20 mV) in different Ag/AgCl REs with the same LiCl-KCl-AgCl salt composition in the RE were sometimes observed. Because each potentiometry sensor will be calibrated by measuring the OCP of different LiCl-KCl-GdCl₃ salts with known compositions to obtain the equation (in a general form) of OCP vs GdCl₃ concentration:

$$OCP = A + B \cdot \log X_{GdCl_3},$$

where A and B are constant at a given temperature and $X_{GdCl_3}$ is the molar fraction of GdCl₃, a small variation between different Ag/AgCl REs is expected not to significantly affect the GdCl₃ concentration measurement.

In this study, the addition of NdCl₃ likely affected the Gd/GdCl₃ equilibrium by reacting with the Gd metal "dissolved" in the salt or reacting with the Gd electrode, and change the GdCl₃ concentrations. This may have some implications for potential application of potentiometry measurements. Since one goal of the potentiometry study using GdCl₃ salt as surrogate is for monitoring the UCl₃ concentration in LiCl-KCl-UCl₃ salt for uranium electrorefining. Based on the successful results using GdCl₃ surrogate salt, it is hypothesized that by measuring the OCP between a U electrode and Ag/AgCl RE, the UCl₃ concentration can be measured. Generally, in the LiCl-KCl-UCl₃ salt for uranium electrorefining, there are no other salts that have higher Gibbs free energy of formation than UCl₃. But if some salts that have higher Gibbs free energy of formation than UCl₃ were added to the molten salt vessel for electrorefining, they will react with the uranium (anode and cathode) in the vessel, and the U electrode for the potentiometry sensor as well, leading to UCl₃ concentration increase, and thus OCP increase. This scenario is a deviation of the normal electrorefining operation, which should be avoided. Luckily, this scenario can be detected by the potentiometry using U electrode vs Ag/AgCl RE, suggesting that the potentiometry sensor can also be used as a monitor for ensuring normal operation of the uranium electrorefiner.

In this study, the GdCl₃ concentration range in LiCl-KCl-GdCl₃ salt is 0.0005 to 0.014 molar fraction. At this range, the activity coefficient of GdCl₃ is constant, but caution is needed when extending the application beyond this range.

Summary

In a LiCl-KCl-GdCl₃ salt system, when there are no other active chlorides present, the potentiometry measurement using Gd metal and a Ag/AgCl RE can be used to measure the GdCl₃ concentration and calculate the activity coefficient of GdCl₃ salt in the tested GdCl₃ concentration range of 0.0005 to 0.014 molar fraction.

The addition of LaCl₃ and CeCl₃ had no apparent effect on the activity of GdCl₃ in the LiCl-KCl-GdCl₃ salt system. However, for reasons not completely understood, NdCl₃ did affect potentiometry measurements conducted on the LiCl-KCl-GdCl₃ salt, though the reaction between Gd electrode and NdCl₃, which probably occurred after the NdCl₃ addition, is considered the likely cause.

The Gd metal can be dissolved in LiCl-KCl-GdCl₃ salt. To achieve an accurate analysis of the GdCl₃ concentration in the salt by ICP-MS, the contribution of dissolved Gd metal needs to be removed.

The potentiometry measurements in the present study cover only LiCl-KCl-GdCl₃ salts with 0.0005 to 0.014 molar fraction GdCl₃, so caution is needed when extending beyond that range. While the main purpose of this study was to evaluate the feasibility of using potentiometry for GdCl₃ concentration monitoring in a LiCl-KCl-GdCl₃ salt system, the results herein may also be helpful in understanding molten salt chemistry and thermodynamics.

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Table I. Salt compositions (in molar fraction) after experiments analyzed by ICP-MS and comparison with calculated values.

| Salt component | Calculated concentration in molar fraction based on salts added in experiments | Measured concentration in molar fraction by ICP-MS | Difference Percentage (%) |
|----------------|--------------------------------------------------------------------------------|-----------------------------------------------|---------------------------|
| GdCl₃          | 0.0136                                                                         | 0.0155                                       | +14.2                     |
| LaCl₃          | 0.00142                                                                        | 0.00140                                      | –0.9                      |
| CeCl₃          | 0.00272                                                                        | 0.00272                                      | –2.0                      |
| NdCl₃          | 0.0104                                                                         | 0.0105                                       | +0.9                      |

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