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Electrochemistry of Zn and co-reduction of Zn and Sm from LiCl–KCl melt

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Abstract The electrochemical behavior of Zn(II) ions in LiCl–KCl and Sm(III) ions in LiCl–KCl–$ZnCl_2$ melts on a Mo electrode at 773 K was studied by various electrochemical techniques. The results showed that the reduction of Zn(II) to Zn(0) consisted of a one-step process. The electrode reaction of LiCl–KCl–$ZnCl_2$ solutions indicated that the under potential deposition of Sm on pre–deposited Zn electrode formed three kinds of Zn–Sm intermetallic compounds at electrode potentials around −1.57, −2.17 and −2.29 V. The electrochemical extraction of samarium was carried out in LiCl–KCl–$ZnCl_2$ melts on a Mo electrode at 773 K by potentiostatic electrolysis (−2.3 V) for 40 h with an extraction efficiency of 99.87%. Zn–Sm bulk alloy was obtained by galvanostatic electrolysis. The microstructure and micro–zone chemical analysis of Zn–Sm alloy were characterized by X–ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

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Introduction

Nowadays, the traditional hydrometallurgical process is no longer available for extraction of lanthanides (Lns) and actinides (Ans) because of their low solubilities in an aqueous medium.[1] Pyrochemical separation processes using molten salts have been proposed as an alternative approach for extracting lanthanides and actinides from the fission products because of their high thermal resistance, high radiation resistance and high solubility of molten salts.[2–4]

Sm is a typical element of fission products. In principle, since the reduction potential of Sm(II) to Sm(0) is more negative than that of the solvent in the chloride system,[5] it is impossible to extract Sm metal directly by electrolysis from molten salt chlorides. The only technique for extracting Sm metal is by a shift to a more positive potential on active electrodes.[6,7]

Some researchers have been interested in the extraction of lanthanides with variable valence. Castrillejo et al.[8,9] have extracted Yb and Sm on a reactive Al cathode in LiCl–KCl melts. Massot and co–workers[10,11] have also extracted Nd on reactive cathodes (Cu and Ni) in LiF–CaF_2 melts at 920 ℃. The extraction efficiencies were found to be more than 99.8% on both reactive electrodes. Smolenski et al.[12] extracted Tm on a reactive Al cathode in NaCl–2CsCl melts. Massot et al.[2] have investigated the Sm extraction in LiF–CaF_2–AlF_3 melts and calculated the extraction efficiency (99.4%). Massot and co–workers[13] have also extracted Eu on a reactive cathode (Al, Cu) in LiF–CaF_2 melts at 840 ℃. Electrochemical extractions resulted in an

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extraction efficiency of about 92% for copper electrode, and 99.7% for co-reduction with aluminium ions.

The reduction potentials of lanthanides were more positive than that of Li^+ on an inert electrode. To extract lanthanide completely from solvent, we need to minimize the ultimate concentration of lanthanide metal by controlling the electrode potential. The electroextraction (electrolytic separation) efficiency can be defined as

$$\eta = 1 - \frac{\alpha_{final}}{\alpha_{initial}} \tag{1}$$

Where α_{final} and $\alpha_{\mathrm{initial}}$ are the molarities of lanthanide after and before electroextraction. According to the equation of Nernst, the theoretical potential differences decided by the initial and ultimate concentration of lanthanides we need to extract.

$$\Delta E = E_{initial} - E_{final} = \frac{RT}{nF}\ln\frac{\alpha_{initial}}{\alpha_{final}} = \frac{RT}{nF}\ln\frac{1}{1-\eta} \tag{2}$$

where R is the universal gas constant, T is the absolute temperature in K, n is the number of exchanged electrons, and F is Faraday's constant (96485 C mol^{-1}). From formula (2), the reduction potential difference of lanthanide (it is the reduction potential difference of lanthanide and Li on inert electrode in LiCl–KCl melts) depends on electron transfer number and extraction efficiency, that is, the extraction efficiency is closely related to the reduction potential difference. The theoretical potential differences we need to achieve are listed in Table 1, when the electrolytic extraction efficiency η is in the range of 99%～99.999%.[14]

From Table 1 we see that we need to enlarge the precipitation potential difference between lanthanide and metal ion in solvent to realize the complete electroextraction

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of lanthanide. Because the reduction potential of lanthanide is close to that of Li^+, the complete extraction (separation) of lanthanide on an inert electrode is hard to achieve. Some lanthanide metals cannot, however, be obtained by electrolysis on an inert electrode (because the deposition potential of lanthanide metal is more negative than that of the solvent). Because the activity of lanthanide will decline on an activated cathode, electrodeposition of lanthanide on active electrode will have a more positive deposition potential than on an inert electrode (that is, the depolarization effect).

Due to the increase of potential difference between lanthanide and Li on Al cathode, electrochemical extractions of lanthanides on Al cathode were extensively investigated. Massot and co–workers[1] have extracted Nd on Al cathode in LiF–CaF_2 melts at 860℃, of which the extraction efficiency was more than 95%. They have also investigated Ce extraction on pre–deposited Al cathode in LiF–CaF_2–AlF_3 melts and calculated the extraction efficiency to be 99.5%.[2] Yan et al.[15] investigated the electrochemical extraction of Pr in the form of Al–Pr and Al–Li–Pr alloys from LiCl–KCl eutectic melts by potentiostatic and galvanostatic electrolysis at 500 ℃. Zhang et al.[16] studied the electrochemical extraction of thorium from LiCl–KCl molten salts by forming Al–Th alloys at 680 ℃. Shi et al.[17] carried out an electrochemical extraction of Gd from Gd_2O_3 in LiCl–KCl–$AlCl_3$ molten salts. The electrochemical extraction of gadolinium was performed by co-reduction with Al^{3+} on the aluminum electrode with an extraction efficiency of 89.7% for potentiostatic electrolysis and 96.5% for galvanostatic electrolysis, respectively.

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From the references above, most researchers have employed Al as a cathode to extract lanthanides. In this paper, a zinc cathode was applied to extract Sm. As we know, the deposition potential of zinc ion is more positive than that of aluminium ion in molten chlorides. The deposition potential of lanthanides on a zinc cathode will be more positive than that of lanthanides on an aluminium cathode, which means that the deposition potential difference between lanthanides on zinc cathode and Li will further increase. The deposition potential difference is larger, and the extraction efficiency is higher. Another factor to be considered is that Zn has a lower melting point (692 K) and boiling point (1180 K) in comparison with Al. Consequently, electrolysis can be carried out at a relatively low temperature. In addition, a lower boiling point facilitates the separation between Zn and Sm. Moriyama et al.[18–20] evaluated separation coefficient of actinides and lanthanides on a liquid zinc electrode in LiF–BeF_2 system, the results show that, liquid zinc as the cathode extract actinides and lanthanides from the molten chloride salts is feasible. Recently, our group has successfully extracted Tm on zinc cathode.[21] Shi et al.[22] investigated the co-reduction of Sm(III) and Zn(II) ions on the Mo electrode and the under potential deposition of Sm(III) ions on the liquid Zn electrode. They found that the recovery rate of Sm from the LiCl–KCl–$SmCl_3$(2 wt.%) melt can reach to 94.5% by the electrolysis on the liquid Zn electrode. As far as we know, few studies on the electrochemical behavior of Zn(II) ion in molten LiCl–KCl have been reported in the literature.[23,24] In this paper, the electrochemical behavior of Zn(II) ion on a molybdenum electrode in molten LiCl–KCl was investigated by various electrochemical techniques, and direct

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electrochemical extraction of samarium by co-reduction with zinc in LiCl–KCl molten salt was studied. The extraction efficiency of Sm was evaluated as well.

Experimental

Preparation and purification of the melts

The mixture of LiCl–KCl (63.7:36.3 mol%, analytical grade) was dried under vacuum for more than 48 h at 523 K to remove excess water. And then the mixture was melted in an alumina crucible placed in a quartz cell located in an electric furnace. The melts temperature was measured by a nickel-chromium thermocouple sheathed by an alumina tube. Metal ion impurities of the melts were removed by pre–electrolysis at −2.1 V (vs. Ag/AgCl) for 3 h. Zinc and samarium elements were introduced into the bath in the form of dehydrated $ZnCl_2$ and $SmCl_3$ powder. Since Ln ions are very sensitive to O^{2-} ions, to avoid generating SmOCl or Sm_2O_3, HCl was bubbled through to purify the melts and then argon was bubbled to remove excess HCl.[25]

Electrochemical apparatus and electrodes

All electrochemical techniques were performed using an Autolab PGSTAT 302N electrochemical workstation (Metrohm Co., Ltd.) with a Nova 1.8 software package. The working electrodes were molybdenum wires (d=1 mm, 99.99% purity), which were polished thoroughly using SiC paper, and then cleaned ultrasonically with ethanol prior to use. The counter electrodes were graphite rods (d=6 mm, 99.99% purity). The active electrode surface area was determined by measuring the immersion

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depth of the electrode in the melts. The reference electrode was a silver wire (d=1 mm) which dipped into a Pyrex tube containing a solution of AgCl (1wt.%) in LiCl–KCl (63.7:36.3 mol%) melts. All potentials were referred to this Ag/AgCl couple.

Auxiliary techniques

The Zn–Sm alloy was prepared by galvanostatic electrolysis at 973 K. After electrolysis, the alloy sample was extracted from the melts and washed in hexane (99.8% purity) in an ultrasonic bath to remove salts. All operations were carried out under an argon atmosphere. The treated sample was stored in the glove box for analysis. The deposit was analyzed by XRD (X' Pert Pro; Philips Co., Ltd.) using Cu–Kα radiation at 40 kV and 40 mA. The specimen was mounted in thermosetting resins using a metallographic mounting press and then mechanically polished. Then, the microstructure and micro–zone chemical analysis were measured using SEM and EDS (JSM–6480A; JEOL Co., Ltd.). The concentrations of K(I), Li(I), Sm(III), and Zn(II) were analyzed using an inductively coupled plasma atomic emission spectrometer (ICP–AES, IRIS Intrepid II XSP, Thermo Elemental). The samples were taken from the clear supernatant fluid in the molten salt mixtures before and after electrolysis. After the clear supernatant fluid samples were solidified, each sample was dissolved in distilled water for analysis. The solution was diluted and analyzed using an ICP-AES. The contents of K(I), Li(I), Sm(III), and Zn(II) measured by ICP were converted to the masses of KCl, LiCl, $ZnCl_2$, and $SmCl_3$, and then the concentrations of zinc and samarium before and after electrolysis were calculated.

Results and discussion

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Electrochemical behavior of Zn(II) in LiCl–KCl melts on a molybdenum electrode

Cyclic voltammetry

Cyclic voltammetry was performed on a molybdenum electrode in LiCl–KCl (63.7:36.3 mol%) melts (Fig. 1). Curve 1 represents the voltammogram before the addition of $ZnCl_2$. Only one cathodic signal E is observed from approximately −2.37 V which is associated with the deposition of lithium, and the corresponding anodic signal E′ is related to the dissolution of lithium. Curve 2 shows the voltammogram with the addition of $ZnCl_2$. In curve 2, prior to the cathodic signal E, another cathodic peak A (about −0.74 V) is seen and attributed to the reduction reaction of Zn(II) to Zn(0):

$$\mathrm{Zn}\left(\mathrm{II}\right)+2\mathrm{e}^{-}\rightarrow \mathrm{Zn}\left(0\right) \tag{3}$$

In the positive–going scan, anodic peak A′ is attributed to the anodic oxidation process of the reaction. The increase of cathodic current from about −2.33 V is attributed to the underpotential deposition of Li on pre-deposited Zn to form Li–Zn alloy.

Fig. 2 exhibits the CV attained in LiCl–KCl–$ZnCl_2$ (9.5×10^{-5} mol·cm^{-3}) melts on a molybdenum electrode at various scan rates at 773 K. From Fig. 2, ΔE_P ($\Delta E_P=\left|E_{pa}-E_{pc}\right|$) increases markedly with increasing sweep rate; ΔE_P is larger than the value of 2.3RT/nF or 0.076 V for a two–electron reaction at 773 K. These results reveal that the deposition/dissolution reaction of Zn(II) ion is not completely reversible. There are two linear relationships between cathodic peak current (I_P) and

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the square root of scan rate ($v^{1/2}$), at low and high scan rates, respectively (Fig. 3). As a whole, the relationship between I_P and $v^{1/2}$ presents a transition from reversible to quasi–reversible and ultimately irreversible behavior. To further examine the reversibility of the electrode reactions, the dependencies of the cathodic and anodic peak potentials on the logarithm of the sweep rate are recorded (Fig. 4). Up to scan rates of 0.15 V s^{-1}, the value of peak potential, E_P, is consistent and independent of the sweep potential rate. Whereas for higher sweep rates, the values of the anodic and cathodic peak potentials shift slightly towards the positive and negative ones, respectively. These results display that the reduction of Zn(II) is quasi–reversible.[26]

Square wave voltammetry

Since square wave voltammetry is more sensitive and has a higher resolution than cyclic voltammetry,[27–29] it was adopted to further examine the electrochemical behavior of Zn(II). Fig. 5 displays the square wave voltammogram of a solution of $ZnCl_2$ at a step potential of 5 mV. One peak (peak A) at around 0.72 V is derived from the one–step reduction reaction of Zn(II) to Zn(0).

The width of the half peak ($W_{1/2}$) depends on the number of electrons transferred and on the temperature, and is calculated as follows:

$$W_{1/2} = 3.52\frac{RT}{nF} \tag{4}$$

where R, T, F, and n have the same meanings and units as described in Equation 2. To prove the reduction potential of Zn ions is −0.72 V, the number of electrons involved in this electrochemical step is determined by estimating the width of peak A at half of its height by Eq. (4).[28] The Gaussian fitting model is applied to process the curve

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(inset figure). Analysis of the obtained curves give the number of electrons (n=2.1) involved in the electrochemical reduction reaction of peak A, which is approximately equal to 2. This value confirms that peak A originates from the reduction reaction of Zn. The square wave voltammogram results are in agreement with the cyclic voltammograms results.

Electrochemical behavior of Sm(III) in LiCl–KCl–ZnCl$_2$ melts on a molybdenum electrode

Cyclic voltammetry

Cyclic voltammetry with different potential windows is performed at 773 K in LiCl–KCl–SmCl$_3$ (2.5×10^{-4} mol·cm^{-3})–ZnCl$_2$ (8.5×10^{-5} mol·cm^{-3}) system (Fig. 6). The scanning potential limits of the four cyclic voltammograms are −1.8, −2.2, −2.4 and −2.5 V, respectively. We can distinguish a corresponding situation between the oxidation and reduction peaks through different potential scanning limitations. In Fig. 6, two pairs of corresponding redox peaks A/A' and B/B' appear when the cathode limit reaches −1.8 V, excluding the A/A′ system at nearly −0.79/−0.59 V, corresponding to the deposition and subsequent reoxidation of zinc, cathodic peak B at roughly −1.56 V, are attributed to the formation of Zn–Sm intermetallics; when scanning the limit to −2.2 V, a pair of corresponding reduction/oxidation peaks C/C' occur, cathodic peak C at roughly −2.16 V, are attributed to the formation of another Zn–Sm intermetallics; when scanning the limit to −2.4 V, in addition to the redox peaks A/A', B/B' and C/C', redox peaks D/D' are also detected, cathodic peak D at roughly −2.29 V, are attributed to the formation of a third Zn–Sm intermetallics, the

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under potential deposition of samarium on pre–deposited zinc film results in the formation of Zn–Sm alloys; when scanning the limit to −2.5 V, the last couple of E/E' corresponding to the reduction and oxidation of Li metal is observed.

Square wave voltammetry

Fig. 7 shows a square wave voltammogram of the LiCl–KCl–$ZnCl_2$ (8.5×10^{-5} mol·cm^{-3})–$SmCl_3$ (2.5×10^{-4} mol·cm^{-3}) melts on a molybdenum electrode at a step potential of 5 mV and frequency of 10 Hz at 773 K. There are four apparent peaks at −0.76, −1.48, −2.09, −2.24 V corresponding to the formation of pure Zn metal and three different Zn–Sm alloys, respectively. The results of square wave voltammogram are in agreement with the ones attained from the cyclic voltammograms (Fig. 6).

Chronopotentiometry

Fig. 8 presents chronopotentiograms measured on a molybdenum electrode (S=0.332 cm^2) in LiCl–KCl–$ZnCl_2$ (8.5×10^{-5} mol·cm^{-3})–$SmCl_3$ (2.5×10^{-4} mol·cm^{-3}) melts at various current intensities. The first plateau at –0.73 V marked 1, at a cathodic current lower than –20 mA, is associated with the reduction of Zn(II). Another three plateaus labeled 2, 3, and 4, observed at –1.52, –1.96, and –2.24 V, correspond to the formation of three kinds of Zn–Sm alloys. When the applied current is raised to –60 mA (–0.18 A/cm^2), the potential plateau is approximately –2.39 V (plateau 5). At this current intensity, the codeposition of Zn and Sm occurs. The last plateau 5 is ascribed to the deposition of Li on Mo electrode. It is clear that the potential regions for deposition of Zn and Sm are close to those observed in the cyclic voltammograms.

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Open circuit chronopotentiometry

Fig. 9 shows a typical open–circuit chronopotentiogram obtained from LiCl–KCl–$ZnCl_2$ (8.5×10^{-5} mol·cm^{-3})–$SmCl_3$ (2.5×10^{-4} mol·cm^{-3}) melts on a Mo electrode at 773 K. There are five plateaus at roughly: (1) −2.38 V, (2) −2.15 V, (3) −1.88 V, (4) −1.42 V, (5) −0.80 V.

Plateau 1 is the equilibrium potential plateau of Li(I)/Li. Plateau 5 is derived from the rest potential of the Zn film. Since Zn previously deposited on the molybdenum, the deposited Sm metal reacts with Zn and diffuses into the Zn substrate. This phenomenon results in the electrode potential gradually shifting to more positive values. During this process, a potential plateau is observed when a composition of the electrode surface is within a two–phase coexisting state.[8,30,31] Therefore, plateaus 2, 3, and 4 are related to the formation of three different Zn–Sm intermetallic compounds.

Potentiostatic electrolysis and electrolytic extraction of samarium ions by co-reduction

The zinc firstly coats on to the molybdenum cathode to construct a zinc cathode. This conduces the deposition potential of samarium ions to move in a more positive direction by co-reduction with Zn(II) ions. This so–called “depolarization effect” allows the theoretical extraction efficiency of the lanthanides to be enhanced up to 100%.[8] Based on the results of electrochemical studies, electrolytic extraction of samarium ions by co-reduction with Zn(II) ions was implemented via potentiostatic electrolysis in LiCl–KCl–$ZnCl_2$ (1.3×10^{-4} mol·cm^{-3})–$SmCl_3$ (1.7×10^{-4} mol·cm^{-3}) melts on a molybdenum electrode. In light of the results of cyclic voltammograms and square wave voltammogram, we chose the potential of the co–reduction peak at about −2.3 V as the electrolysis potential. The extraction process is followed by drawing square wave voltammograms at different times to monitor the electroactive species content of molten salts. Furthermore, when measuring a new square wave voltammogram, a new molybdenum cathode should replace the last one to ensure the accuracy of the results.

Fig. 10 shows a serial of square wave voltammograms measured in the extraction process. We observe that the current density decreases remarkably from the square wave voltammograms. The current density decreases more quickly at the initial stage than at the subsequent one in the electrolysis process. After 40 h electrolysis, the current density is close to zero.

To assess the extraction efficiency of the extraction process, the concentrations of Li, K, Zn and Sm elements in the melts after potentiostatic electrolysis for 40 h were measured by ICP. The weight percent of LiCl, KCl, $ZnCl_2$ and $SmCl_3$ of the melts after potentiostatic electrolysis were calculated to be 47.18%, 52.79%, 0.022% and 0.0019%, respectively. Consequently, the extraction efficiency is evaluated by Eq. (1). Where $\alpha_{initial}$ is the initial concentration of Sm(III) in the melts, and α_{final} is the final concentration of Sm(III) in the melts. The extraction efficiency of the samarium ion is computed to be 99.87%. Combined with the initial concentrations of $ZnCl_2$ and $SmCl_3$ and the extraction efficiency, Sm should be extracted in the form of Sm-Zn alloy and Sm solid solution after potentiostatic electrolysis for 40 h since no alloy with Sm composition higher than Zn exists in Sm–Zn binary alloy system.

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Galvanostatic electrolysis and characterization of the deposits

Alloys prepared at a low temperature are always residue–shaped and high temperature is beneficial for the aggregation of alloys: therefore, galvanostatic electrolysis (−1.95 A) was executed for 2.5 h in LiCl–KCl–$ZnCl_2$ (1.3×10^{-3} mol·cm^{-3})–$SmCl_3$ (1.3×10^{-4} mol·cm^{-3}) melts on a molybdenum electrode at 973 K. Fig. 11 shows the X–ray diffraction pattern of an alloy sample obtained by galvanostatic electrolysis from the LiCl–KCl–$ZnCl_2$ (1.3×10^{-3} mol·cm^{-3})–$SmCl_3$ (1.3×10^{-4} mol·cm^{-3}) melts. The XRD pattern of the sample shows the formation of Sm_2Zn_{17}, LiZn and Zn phases. With the extension of electrolysis time, Sm could be extracted in the form of Sm-Zn alloy and Sm solid solution.

To inspect the distribution of Zn and Sm elements in the alloy obtained by galvanostatic electrolysis from the LiCl–KCl–$ZnCl_2$ (1.3×10^{-3} mol·cm^{-3})–$SmCl_3$ (1.3×10^{-4} mol·cm^{-3}) melts, SEM and EDS mapping analysis of the alloy sample were performed (Fig. 12). From the SEM image, a large number of small lumpy precipitates are seen on the surface of the alloy. One random block was taken, magnified (from the red circle), and examined with EDS mapping analysis. From the mapping analysis of elements, we find that Sm element mainly distributes in the white zone in the SEM photograph of the alloy. To further investigate the distribution of Sm, EDS quantitative analysis was carried out. The EDS results of the points marked 1, 2 and 3 taken from the white zone and black zone show that the deposit is made up of elements Zn and Sm. At the same time, the results of the EDS demonstrate that the white zone dissolves more Sm (39.01 mass% at point 3) than the black zone (0.87

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mass% at point 2).

Conclusion

The electrochemical behavior of Zn(II) ion on a molybdenum electrode in molten LiCl–KCl–$ZnCl_2$ at 773 K was investigated by various electrochemical techniques. We proved that Zn(II) was reduced to Zn metal by a one–step process, that is, Zn(II)+2e$^-$→Zn(0). The electrochemical reductions of Zn(II) to Zn(0) were found to be quasi–reversible. The extraction of Sm(III) ion by co-reduction with Zn(II) ion in LiCl–KCl–$ZnCl_2$–$SmCl_3$ melts on an inert electrode at 773 K was found to be feasible. The extraction efficiency of Sm(III) was estimated to be 99.87% after potentiostatic electrolysis for 40 h. This co-reduction process can indeed be used for other electrochemical systems for extraction of lanthanides and alloy preparation. According to the co–reduction mechanism, Zn–Sm alloy with Sm_2Zn_{17} phase was obtained directly via co–reduction of Zn, Sm on an inert electrode in molten LiCl–KCl–$ZnCl_2$–$SmCl_3$ melts.

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