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Kinetics of the actinides–lanthanides separation: mass transfer between molten fluorides and liquid metal at high temperatures

Florent Lemort [a,*], Roger Boen [a], Michel Allibert [b], Damien Perrier [c], Yves Fautrelle [c], Jacqueline Etay [c]

[a] *Commissariat à l'Énergie Atomique, CEA-Marcoule, BP 171, 30207 Bagnols-sur-Cèze cedex, France*
[b] *LTPCM-ENSEEG, BP 75, 38402 Saint Martin d'Hères, France*
[c] *CNRS-EPM-Madylam – ENSHMG BP 95 – 38402 St Martin d'Hères cedex, France*

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Abstract

Experimental studies on the extraction of actinides and other elements from a fluorinated salt into a liquid metal phase containing a reducing agent such as magnesium or aluminium have been performed using two different systems. The rate of transfer is very rapid and could, depending on the way stirring is carried out, vary with the stirring rate. Three different types of stirring have been tested and observations are explained both in terms of hydrodynamics and chemistry. The role of interfacial agitation is discussed and the assumption that the limiting factor is related to the chemical reaction and not mass transfer is confirmed by a measured activation energy of 180 kJ mol^{-1}. Thermal effects are observed with different magnitudes depending on the reduced species. Chemical control of the kinetics combined with thermal effects account for the rapid transfer. These results can be used to develop a high-temperature process for separating actinides and lanthanides. More work is required to determine the reaction mechanisms, which may not be limited to the interface.

1. Introduction

Studies of high-temperature material transfer kinetics involving chemical reactions in two-phase liquid systems have shown that they are generally controlled by diffusion in the transfer boundary layer [1]. Stirring of the system is thus a major factor in controlling the reaction rate. This is the case, for example, in metallurgical applications.

The present paper focuses on the kinetics of the transfer of an element M from a fluorinated phase into a metallic phase. MF_x is reduced by a reducing agent R. This process is shown in Fig. 1 and corresponds to the oxygen–reduction reaction, expressed for one mole of F_2 as

$$\frac{2}{x}MF_x + \frac{2}{y}R \leftrightarrow \frac{2}{x}M + \frac{2}{y}RF_y. \quad (1)$$

The transfer coefficient k_j is determined by measuring the concentration of R or M in the saline or metallic phase.

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[*] Corresponding author.

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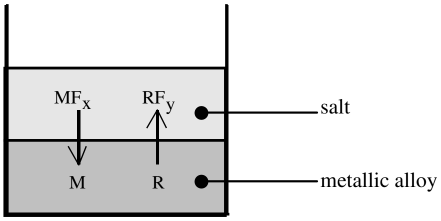

Fig. 1. Sketch of the mass transfer of species by an oxygen–reduction reaction between a metallic alloy and a mixture containing fluorinated salt.

In order to compare results from various experiments, we assume that the concentration $C_j(t)$ of a compound j in the corresponding phase varies with time according to the following relationship:

$$\frac{dC_j}{dt}(t) = k_j \frac{A}{V_j}(C_j^i - C_j(t)), \qquad (2)$$

where A, V_j, and C_j^i are respectively the area of the interface, the volume of the phase in which the compound j is present and the concentration of this compound at the interface.

Eq. (2) introduces the capacity time $T_{\mathrm{ca},j}$ characteristic of the transfer of one element j in its phase and is defined as

$$T_{\mathrm{ca},j} = \frac{V_j}{k_j A}. \qquad (3)$$

Assuming that the concentration of an element is always equal to its equilibrium concentration, the integration of Eq. (2) leads to the conventional equation:

$$\mathrm{Ln}\left(\frac{C_j - C_j^e}{C_j^0 - C_j^e}\right) = -k_j \frac{A}{V_j} t = -\frac{t}{T_{\mathrm{ca},j}}, \qquad (4)$$

where C_j^e is the equilibrium concentration taken as the concentration at the end of the test and C_j^0 is the concentration at the starting time. Within the framework of the film theory, the plot of $\mathrm{Ln}((C(t) - C^e)/(C^0 - C^e))$ versus time must give a line with a slope proportional to the transfer coefficient.

It appears that in the case of the transfer of actinides from a fluoride mixture, characterized by a rather complex transfer mechanism, the variation of the concentration of the species with time is probably not as simple as that which is described by Eq. (2). Nevertheless, the kinetic study presented in this paper will use the concept of capacity time to describe the transfer kinetics of zirconium and uranium (a surrogate of the actinides) from the fluorinated salt towards a metal. Details on the use of Eq. (4) are provided in Appendix A.

When transfer is controlled by the chemical reaction, k_j represents the kinetic constant of the chemical reaction involving species j. This constant is temperature-dependent according to an Arrhenius law. When the transfer is controlled by diffusion, k_j corresponds to the mass-transfer coefficient for species j (often written as h_j).

We investigated the transfer kinetics of the actinides and lanthanides from a fluorinated salt phase into a metal phase including a reducing agent. By monitoring the concentrations in one of the phases during the exchange and interpreting the results based on Eq. (4), we are able to demonstrate that:

- stirring plays an important role,
- material transfer at the interface does not appear to be the only limiting factor.

The latter observation is rare in literature related to this type of process. For instance, some previous studies [5] have shown that the reduction of neptunium by lithium dissolved in liquid bismuth is very long, leading to the assumption that the kinetics are limited by diffusion phenomena.

2. Principle and experimental method

To obtain kinetic data, experiments were performed on two complementary systems. The tests carried out respectively with the first and second systems are summarized in Table 1.

The first system was used to study the kinetics of reduction and transfer for LaF_3, SmF_3, UF_4, ZrF_4, and CrF_3. Each compound was first dissolved at a concentration of 4 mol% in the LiF–CaF_2 eutectic at 720 °C.

Table 1
Characteristics of the tests carried out using the two systems

	System 1	System 2
Metal/salt	Zn–Mg/LiF–CaF_2	Al–Cu/LiF–CaF_2–MgF_2
Transferred element	Sm–La–Zr–Cr–U	Zr
Crucible diameter (mm)	40	90
Stirring technology	Mechanic paddle	Two-frequency magnetic field
Heating technique	Furnace	Induction
Sampling	Metal or salt	Metal