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HIGH TEMPERATURE CHEMICAL ENGINEERING RESEARCH IN NUCLEAR TECHNOLOGY

Donald R. Olanier, J. Camahort, and A. Pasternak

June 1965
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High temperature non-aqueous reprocessing of spent nuclear fuels has received considerable attention in recent years, and in some instances such processes can compete favorably with the conventional aqueous methods. While considerable effort has been devoted to the thermodynamics of high temperature processing, their kinetics have received little attention. This paper will report the results of kinetic experiments on typical volatility and pyrometallurgical systems.

The Chlorination of UCl₄ by Cl₂

The purpose of this study was to investigate the diffusional and chemical rate phenomena associated with the reaction:

\[ \text{UCl}_4(\text{l}) + \text{Cl}_2(\text{g}) = \text{UCl}_6(\text{l}) \]  

(1)

The reaction was carried out between gaseous chlorine and UCl₄ dissolved in the eutectic LiCl-KCl mixture (59 mole % LiCl). The eutectic melts at 350°C, and the experiments were carried out in the range of 400-700°C. At these temperatures the hexachloride is volatile, and depending upon the conditions of the reaction, may appear either as a gaseous or a dissolved species. Some UCl₅ was probably produced by the reaction. The analytical technique measured only the increase in the oxidation state of the uranium in solution, and did not differentiate between UCl₅ and UCl₆.

To aid in interpreting the kinetic data, the solubility of chlorine in the pure LiCl-KCl was measured. The amount of dissolved...
chlorine at 400 and 500°C was found to be less than $4 \times 10^{-9}$ mole/cc-atm. Since chlorine is essentially insoluble in the salt phase and the UCl$_4$ has a negligible vapor pressure reaction (1) can take place only at the gas-liquid interface, and not in either bulk phase.

The equilibrium constant of reaction (1) was measured by sparging Cl$_2$ into a 2 w/o solution of UCl$_4$ in the fused salt and measuring the ratio of tetravalent to total uranium. The results could be expressed by:

$$\ln K = 2.65 - \frac{2730}{T}$$

(2)

where $K$ is the equilibrium constant in atm$^{-1}$. The reaction is endothermic with a heat of reaction of 5.4 kcal/mole and quite reversible. Conversion of U$^{4+}$ to the hexachloride is incomplete at all temperatures studied; the U$^{4+}$/U$_{tot}$ ratio was 0.800 at 400°C and 0.612 at 600°C.

The reversibility of the reaction is important in analysis of the kinetics.

The primary criterion in selecting a contacting device for the kinetic studies was knowledge of the hydrodynamics of the gas and liquid phases. If the velocity fields in both phases are known, the associated diffusion problems can be solved. Diffusional resistance can be theoretically extracted from overall rate measurements to reveal any chemical kinetic limitation.

The device selected was the wetted rod contactor shown in Fig. 1. It was constructed of quartz to prevent corrosion due to chlorine and fused salt at temperatures as high as 700°C. The apparatus consists of an upper chamber into which the salt is charged, a lower chamber in which the melt is contacted with chlorine, and a collector at the bottom. The 3mm diameter central rod is seated in a ground fitting between the two chambers. Raising the rod slightly allows the salt to flow smoothly down the rod. The end of the rod terminates in a
section of a funnel whose stem is 3.5 mm inner diameter. It was found by trial and error that a 0.5 mm annulus was sufficient to maintain a liquid level at the top of the stem and thus provide a good seal between the chlorine section and the collecting section. The outlet stem was bathed in HCl gas to prevent oxidation of the U^{+4} by contact with air.

Theoretical analysis showed that the gas phase mass transfer around the moving liquid should be rapid compared to diffusion in the liquid. This was subsequently verified by experiment.

The theory of liquid phase mass transfer on the wetted rod is identical to that for the common wetted wall column. For the case of a constant concentration at the interface, the average outlet concentration is related to the flow rate by:

\[ \bar{c} - c_i = 1 - \left[ 3/3 \pi^{1/6} g^{1/6} \right] (D/\nu)^{1/2} g^{2/3} \]

where \( \bar{c}, \ c_i \) and \( c_o \) are the average outlet, interface and initial concentrations respectively. \( g \) is the acceleration of gravity, \( D \) the liquid diffusivity, \( \nu \) the length of the rod, \( a \) its radius, \( \nu \) the kinematic viscosity of the liquid and \( Q \) the flow rate.

The applicability of Eq. (3) to single mass transfer in film flow down a wetted rod was tested by desorbing CO\(_2\) from water. The results are shown in Fig. 2 and compared to Eq. (3). The 10% discrepancy in the slope of the theoretical and experimental lines is probably due to the stagnant region of the film near the bottom; an effect which has been noted previously in wetted wall columns.

Equation (3) can be applied to an interfacial condition determined by reaction (1) if: (1) the diffusivities of U\(^{+4}\) and U\(^{+6}\) are equal; (2) the product UCl\(_6\) remains in the liquid phase, and (3) the reaction
is assumed to be in chemical equilibrium at the interface. Assumptions (1) and (2) are sufficient to insure that the total uranium concentration is everywhere equal to its initial value; the $U^{4+}$ concentration at the interface can then be computed from the equilibrium constant of Eq. (1). Since gas flow resistance is negligible, the partial pressure of $Cl_2$ at the interface is equal to its known bulk value.

A 2 w/o solution of $UCl_4$ in the fused salt was added to the upper chamber of the contactor and purified by sparging with Zn hydrous HCl gas. The rod was raised slightly and the melt flowed down the rod into a chlorine atmosphere in the lower chamber. Flow rates during the run varied from 12 cc/min to 3 cc/min. Over the 5 minute duration of the run, 5 samples were collected in 1 cc cups, which also served as a means of measuring the flow rate. Experiments were conducted at temperatures between 400 to 700°C, $UCl_4$ concentrations of 1, 2, and 3 w/o, and chlorine partial pressures from 0.25 to 1 atm.

Typical data obtained are shown in Fig. 3, in which $C^*$ is plotted against $1/Q^{2/3}$ as suggested by Eq. (3). It is seen that the extent of reaction is independent of the $UCl_4$ concentration, which demonstrates that the overall process is first order in $U^{4+}$. The effect of chlorine partial pressure could be satisfactorily accounted for by the chlorine pressure dependence of the equilibrium of reaction (1). No effect was noted when the diluent gas at a partial pressure of 0.5 atm was changed from argon to helium. This substantiates the prediction of negligible gas phase resistance, which, if it had been significant, would have changed by ~70% as the gas phase diffusivity changed by a factor of three.

* The diffusion problem can be solved for the more general case of a slow reversible first order reaction at the interface. See Ref. 1.
No volatilization of uranium was noted in any of the rate experiments, although some uranium loss was observed in the equilibrium experiments after long sparyings.

Equation (3) permits the data to be compared directly to theoretical predictions. In Table 1 the slopes of plots such as the one in Fig. 3 are compared to the coefficients of \( 1/q^{2/3} \) of Eq. (3). The agreement is satisfactory in the temperature range 400-500°C, but at higher temperatures the experimental values are considerably smaller than theory. This discrepancy cannot be attributed to a slow chemical step at the interface, since chemical rate limitations usually grow smaller rather than larger as the temperature is increased.

One possible explanation is that the diffusivity of \( U^{+6} \) is considerably smaller than that of \( U^{+4} \). This would cause an accumulation of total uranium at the interface, and to maintain the equilibrium rate of \( U^{+7}/U_{\text{tot}} \), the \( U^{+4} \) concentration would have to increase. The driving force for \( U^{+4} \) transfer would be correspondingly reduced, and the overall conversion decreased.

Another possible source of the deviation is a systematic experimental error in the sampling procedure. The samples were collected in an atmosphere of pure HCl gas in order to prevent contact of the salt with oxygen. In the course of drop formation in the collection zone, the abrupt removal of the chlorine pressure may have caused reaction (1) to reverse, thereby reconverting some of the \( U^{+6} \) formed in the reaction zone to \( U^{+4} \). An analogous effect was observed in studies of \( CO_2 \) absorption in water conducted in the same apparatus. In the latter case, the problem was solved by sampling the liquid with a hypodermic syringe before contact with the atmosphere. Unfortunately, this sampling
TABLE I. Comparison of Experimental and Theoretical Slopes. Data for Pure Cl₂-Initial Uranium Concentration of 2 w/o.

<table>
<thead>
<tr>
<th>T °C</th>
<th>Slope of $\bar{C}^*$ vs $1/Q^{2/3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
</tr>
<tr>
<td>400</td>
<td>0.043</td>
</tr>
<tr>
<td>450</td>
<td>0.055</td>
</tr>
<tr>
<td>500</td>
<td>0.069</td>
</tr>
<tr>
<td>550</td>
<td>0.083</td>
</tr>
<tr>
<td>600</td>
<td>0.097</td>
</tr>
<tr>
<td>650</td>
<td>0.114</td>
</tr>
<tr>
<td>700</td>
<td>0.132</td>
</tr>
</tbody>
</table>
technique cannot be applied to a fused salt because of its high melting point (350°C) and corrosive nature.

Liquid-Metal Extraction

The purpose of this work is to study the kinetics of single drop extraction of a solute metal between two essentially immiscible liquid metal solvents. Interest in this problem is a result of the possible use of the pyrometallurgical process of this type for reprocessing spent reactor fuels.

There has been a steady accumulation of partitioning data for a variety of liquid metal systems, especially those involving uranium and typical fission product metals. The system which has been chosen for this study involves magnesium and the uranium-chromium eutectic (5 w/o Cr) as the immiscible solvents, and lanthanum and barium as the solutes. Distribution data are available for this system.

The use of the uranium-chromium eutectic (MP = 860°C) instead of pure uranium (MP = 1130°C) allows the experiments to be conducted at temperatures considerably below the melting point of uranium. This greatly simplifies the experimental design, since the melting point of uranium is close to the boiling point of magnesium and the system would require pressurization for operation at 1130°C.

Experimental Procedure

The extraction column consists of a graphite crucible 80 cm long and 1.43 cm inner diameter which is closed at the bottom by a machined graphite screw plug (see Fig. 4). The column is inserted in a stainless steel sheath which is fitted with an inert gas flush line at the bottom. At the temperature of the experiments (1000°C) the partial pressure of
Mg is nearly 1/3 atm, and a graphite reflux column placed above the column condenses and returns vaporizing Mg. The entire assembly is placed in a 1.5 m long resistance furnace with 4 individually controlled heating units.

Argon fed into the bottom of the steel sheath passes over niobium wire to remove traces of oxygen and water vapor. The gas then flows up the annular space between the sheath and the extraction column, entering the top of the extraction column by means of grooves in the graphite (dashed lines in Fig. 1), and then rises up the center of the reflux column. This sweep gas prevents oxygen from contacting the molten metals. By reducing the flow rate until no MgO smoke can be seen leaving the top of the column, Mg vaporization losses are maintained at acceptable levels.

The continuous phase was formed by melting a rod of Mg metal in the extraction column. The fission products were extracted from single drops (~ 3 mm diameter) of U-Cr eutectic. Pellets of U-Cr were cut from a large ingot under argon, which kept the surfaces bright. The pellets were sealed in argon-filled quartz capsules during reactor irradiation. Fission products were created in the uranium phase by irradiation for 2 days at a flux of $10^{12}$ n/cm$^2$-sec. A small hole was drilled in the solid U-Cr pellet and the pellets attached to a fine tungsten wire. The pellet was then lowered into the column to a point just under the surface of the molten magnesium. Within ~5 sec, the pellet melted off the wire and dropped to the bottom of the column. The furnace was shut off as soon as the drop had fallen in order to freeze the uranium pellet as quickly as possible. To prevent additional extraction while the molten U-Cr lay at bottom of the column, an inner graphite cup.
containing a 3 cm depth of molten barium chloride (MP 960°C) was placed on top of the screw plug. The uranium drop fell into the salt phase, and the presence of the salt-Mg interface prevented the large end effects which were observed when the pellet remained in contact with Mg during the cooling period.

Pellet sizes ranged from 2 to 4 mm in diameter. Pellets smaller than 2 mm appeared to strike the column walls instead of falling straight through the magnesium. Pellets larger than 4.2 mm broke up, either upon melting off the wire or due to unstable oscillation during fall.

Drag Coefficients

Droplet velocities were measured by placing three collimated scintillation detectors at 20 cm intervals along the column. Each detector output was fed to a high speed rate meter and then to a high speed recorder. The total gamma activity of the irradiated pellets was enough to produce a measurable response in each detector in the ~10 millisecond the pellet spent in front of the collimator. A typical output of the recorder is shown in Fig. 5. The distance between the blips could be converted to a time interval by means of the timing lines automatically inscribed on the recording strip. The time of passage permitted the average drop velocity between the top and middle and the middle and bottom detection points to be measured. The measured velocities were between 60 and 70 cm/sec, essentially independent of pellet size. The velocity in the upper part of the column was ~15% lower than that in the bottom section. The latter was taken to be the terminal velocity. When drop split-up occurred, multiple blips on the recorder outputs were observed. These data were rejected.
Comparison of the data with the correlation of Hu and Kintner \(^4\) developed for low temperature aqueous-organic systems is shown on Fig. 6. Here \(C_D\) is the drag coefficient, \(We\) the Weber number, \(Re\) the Reynolds number and \(P = \sigma_1 \frac{3}{\mu} \cdot \frac{2}{\rho} \cdot \). \(\sigma_1\) = interfacial tension, \(\rho\) and \(\mu\) = density and viscosity of continuous phase. This comparison is of interest because it extends the empirical correlation far beyond the range of some of the parameters involved. The density difference is quite large: 16.5 gms/cc for uranium compared to 1.5 gm/cc for magnesium. The interfacial tension for the U-Mg system has not been measured, but the surface tension of the two elements in the liquid state are known.\(^5\) Using Antonor's rule \((\sigma_1 = \sigma_U - \sigma_{Mg})\), the interfacial tension is 1060 dynes/cm using the rule proposed by Girifalco and Good \(^6\) \((\sigma_1 = \sigma_U + \sigma_{Mg} - 2\sqrt{\sigma_U \sigma_{Mg}})\) a value of 316 dynes/cm is computed. With the larger interfacial tension, the terminal velocities are \(-15\%\) greater than predicted by the Hu and Kintner correlation. The discrepancy is \(30\%\) when the lower value of the interfacial tension is employed. The point in Fig. 6 which exhibits an abnormally low value of the abscissa represents a very small pellet (~ 2 mm) which probably collided with the column wall during fall.

Solute Extraction

The choice of \(La^{140}\) as one of the solutes was determined by the fact that the 1.6 MeV photon characteristic of this nuclide dominates the high-energy end of the gamma spectrum of irradiated \(U^{235}\) after several days of cooling. A spectrum of a typical irradiated U-Cr pellet is obtained with a 400 channel analyzer and is shown in Fig. 7. The easily measurable area under the \(La^{140}\) photopeak is proportional to the amount of the species in the sample. Before an extraction experiment, the activity of \(La^{140}\) in the irradiated pellet was measured.
After the extraction run had been completed, the magnesium ingot was pressed out of the graphite crucible, and the bottom BaCl₂ phase containing the pellet broken off. The La¹⁴⁰ activity of the pellet in the salt phase and of the extracted solute in the magnesium ingot was measured immediately. Since 90% of the La¹⁴⁰ activity remained in the pellet, it proved more accurate to measure the fraction extracted by comparing the activity of the magnesium ingot to the initial pellet activity.

The overall mass transfer coefficient was calculated from the fraction extracted and the measured fall velocities and pellet size:

\[
f = 1 - \exp \left( -\frac{K(A/V)}{d} t \right) \approx \frac{6}{d} K \frac{L}{v}
\]  

(4)

\( f \) is the fraction extracted, \( K \) the overall mass transfer coefficient based upon the U-Cr phase, \( A/V = 6/d \) is the surface-to-volume ratio of the pellet (\( d = \) pellet diameter), \( t = L/v \) is the contact time (\( L = \) column length = 59 cm, \( v = \) fall velocity).

Since the activity of 40 hr La¹⁴⁰ is in part controlled by the presence of its 12.6 day precursor, Ba¹⁴₀, measurement of the rate of decay of the La¹⁴⁰ activity after the experiment permits the fraction of Ba¹⁴₀ extracted to be measured as well.

The experiments were conducted after at least five days following removal of the pellet from the reactor. This interval is sufficient to permit secular equilibrium between Ba¹⁴₀ and La¹⁴⁰ to be established, (i.e. parent and daughter have equal activities), and the decay of the La¹⁴⁰ activity in the irradiated pellet follows the decay law for Ba¹⁴₀, \( a_{La} = a_{Ba} \exp(-\lambda_{Ba} t) \). If in the extraction process, lanthanum and barium were extracted in equal proportions (same fraction extracted), then the
decay of $^{140}\text{La}$ in the magnesium ingot should follow the same $^{140}\text{Ba}$ decay law. If, however, the fraction of the La extracted is greater than that of Ba, the decay of the $^{140}\text{La}$ activity should be more rapid (in the limit of no $^{140}\text{Ba}$ extracted, $a_{\text{La}}$ would decay as $\exp(-\lambda_{\text{La}} t)$).

By considering the radioactive decay equations for the two-member chain, it can be shown that the time dependence of the $^{140}\text{La}$ activity in the Mg ingot after extraction and the ratio of the $^{140}\text{La}$ and $^{140}\text{Ba}$ fractions extracted are related by:

$$\frac{a_{\text{La}}}{a_{\text{La}}^0} = e^{\frac{-\lambda_{\text{Ba}} t}{F}} + (1 - \frac{1}{F})e^{-\lambda_{\text{La}} t}$$  \hspace{1cm} (5)

where

$$F = \frac{f_{\text{La}}}{f_{\text{Ba}}} = \frac{K_{\text{La}}}{K_{\text{Ba}}}$$  \hspace{1cm} (6)

$a_{\text{La}}/a_{\text{La}}^0$ is the ratio of the $^{140}\text{La}$ activity at the time $t$ after extraction to that immediately following extraction. According to Eq. (5), a plot of $(a_{\text{La}}/a_{\text{La}}^0)e^{\lambda_{\text{Ba}} t}$ vs $e^{-(\lambda_{\text{La}} - \lambda_{\text{Ba}}) t}$ should be a straight line whose intercept is $1/F$. A plot of this type is shown in Fig. 8, in which the fraction of $^{140}\text{Ba}$ extracted was only 25% of the fraction of $^{140}\text{La}$ extracted.

Each experiment, then, yields three pieces of information: the velocity of fall, the fraction of lanthanum extracted, and the ratio of lanthanum to barium extracted. If the diffusivities of La and Ba in both phases are assumed equal, these data permit computation of both internal and external mass transfer coefficients, which are related to the overall coefficient by:

$$\frac{1}{K} = \frac{1}{K_i} + \frac{1}{mk_e}$$  \hspace{1cm} (7)
In Eq. (7), \( k_i \) and \( k_e \) are the internal and external mass transfer coefficients and \( m \) is the distribution coefficient (Mg to U-Cr).

The measurements at Ames\(^3\) show \( m_{La} \approx 500 \) (assumed equal to that of cerium) and \( m_{Ba} \approx 5 \). Combining Eqs. (4), (6), and (7) yields:

\[
\frac{k_i}{k_e} = (F-1)(\frac{1}{m_{Ba}} - \frac{F}{m_{La}})^{-1}
\]  

(9)

In Table 2, experimental values are compared with theoretical or empirical correlations developed for aqueous-organic systems. The internal mass transfer coefficients fall between those predicted by the the Handlos and Baron\(^7\) model and those based upon the Hadamard velocity profile in the drop.\(^8\) The external coefficients are much lower than the values predicted by the Griffith and Higbie correlation.\(^9,^{10}\) The abnormally large external resistance, in addition to the considerable scatter in the data, suggests the presence of an irreproducible interfacial resistance. Such a resistance is most probably due to an oxide coat on the pellet, which is extremely difficult to remove from a metal as reactive as uranium. Despite the precautions to prevent contact of the pellet with oxygen, a slight darkening of the pellet surface was observed on the irradiated pellets. To assess this possible source of error, the freshly cut pellets are currently being coated with molten Mg prior to irradiation in the hopes of eliminating the source of oxygen contamination by sealing the pellets as soon as possible.

It should be noted that even though UO\(_2\) is thermodynamically reduced by Mg, there is no assurance that the product MgO is swept free of the
interface during the drop fall or that the reaction is completed in a
time small to the residence time in the column. The only satisfactory
approach is to minimize the extent of surface oxidation initially.
REFERENCES


3. Newsletter of Ames Laboratory, Iowa State University, Reactor Materials and Low Temperature Decontamination Studies (March 1961). Lanthanum distribution coefficients were not reported but were assumed equal to those of cerium because of the chemical similarity of the rare earth elements.


5. Uranium: B. Spriet, Rev. Met. 60, 531 (1963); Mg: V. G. Givov, USAEC Rept. ANL 5749 (1958). σCr has been estimated as 1500 dynes/cm which is the measured value for uranium at the melting point. The U-Cr eutectic surface tension has also been taken as 1500 dynes/cm.


FIGURE CAPTIONS

Fig. 1 Wetted rod contactor (quartz).

Fig. 2 Desorption of CO₂ from water in the wetted rod contactor.

Fig. 3 Chlorination of UCl₄ by pure Cl₂ in the wetted rod contactor, 600°C, various wt. percent UCl₄.

Fig. 4 Graphite column for liquid metal extraction.

Fig. 5 Output of scintillation detector for measurement of drop fall velocities in liquid metal systems.

Fig. 6 Comparison of drag coefficients in the U-Cr eutectic-Mg liquid metal system with the Hu and Kintner correlation.

Fig. 7 Gamma spectrum of irradiated uranium taken with a 400 channel analyzer. Two days irradiation at 10¹² n/cm²·sec and 2.4 day cooling.

Fig. 8 Decay of La¹⁴⁰ activity in magnesium ingot with time after extraction.
12-mm long, 3.5-mm i.d. tubing
6-mm - o.d. tubing
4-mm rod
Ground glass fitting
1"-o.d. tubing
3-mm rod
4"
6"
12-mm o.d. tubing

Fig. 1
Fig. 2
Fig. 4

- S.S. tubing 1\(\frac{1}{2}\)" O.D.
- Graphite reflux column 23" long
- Graphite crucible 31" long
- O.D. 1\(\frac{1}{4}\)"
- I.D. \(\frac{9}{16}\)"
- Support ring
- Niobium wire
Top detector  Middle detector  Bottom detector

Timing lines 0.01 sec

Fig. 5
\( \Delta \sigma_i = 1060 \text{ dynes/cm} \)

\( \circ \sigma_i = 316 \text{ dynes/cm} \)

Fig. 6
Fig. 7
Fig. 8

\[
\frac{N_2^2 e^{\lambda_1 t}}{N_2} \quad e^{-(\lambda_2 - \lambda_1) t}
\]
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