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Reprocessability of molybdenum and magnesia based inert matrix fuels

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Abstract. This work focuses on the reprocessability of metallic ^{92}Mo and ceramic MgO, which is under investigation for (Pu,MA)-oxide (MA = minor actinide) fuel within a metallic ^{92}Mo matrix (CERMET) and a ceramic MgO matrix (CERCER). Magnesium oxide and molybdenum reference samples have been fabricated by powder metallurgy. The dissolution of the matrices was studied as a function of HNO_3 concentration (1–7 mol/L) and temperature (25–90°C). The rate of dissolution of magnesium oxide and metallic molybdenum increased with temperature. While the MgO rate was independent of the acid concentration (1–7 mol/L), the rate of dissolution of Mo increased with acid concentration. However, the dissolution of Mo at high temperatures and nitric acid concentrations was accompanied by precipitation of MoO_3. The extraction of uranium, americium, and europium in the presence of macro amounts of Mo and Mg was studied by three different extraction agents: tri-*n*-butylphosphate (TBP), *N,N*′-dimethyl-*N,N*′-dioctylhexylethoxymalonamide (DMDOHEMA), and *N,N,N*′,*N*′-tetraoctyldiglycolamide (TODGA). With TBP no extraction of Mo and Mg occurred. Both matrix materials are partly extracted by DMDOHEMA. Magnesium is not extracted by TODGA (D < 0.1), but a weak extraction of Mo is observed at low Mo concentration.

Key words: CERCER • CERMET • dissolution • inert matrix fuels (IMF) • liquid-liquid extraction • minor actinides • reprocessing

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Introduction

During the generation of electricity by nuclear power, considerable amounts of short- and long-lived radioactive fission products as well as considerable quantities of bred plutonium (1 wt%) and minor actinides (MA) (0.1 wt%) are generated. Plutonium and MA (especially americium) are of particular concern with respect to long-term radiotoxicity, heat load issues and proliferation risks. The partitioning and transmutation (P&T) of MA in accelerator driven systems (ADS) is one possibility to cope with this problem [1–3].

(Pu,MA)-Oxide within a ceramic MgO matrix (CERCER) and (Pu,MA)-oxide within a metallic ^{92}Mo matrix (CERMET) were proposed as ADS fuel on the basis of various experiments, such as FUTURIX-FTA, HELIOS, BODEX, and ECRIX-H, on the irradiation performance of inert matrix fuels (IMF) with a matrix content >60 vol.% [4–6]. Mo-based fuels showed safety advantages, while MgO-based inert matrix fuels were superior with regard to transmutation performance [7]. The reprocessability of these IMF is under investigation within the EU project ASGARD [8]. The ADS fuel cycle is capable of recycling a high concentration of minor actinides in the fuel. However, multi cycles are needed as well as specific separation processes for the specific fuel. Enriched ^{92}Mo is used because

of its favorable neutronic parameters and needs to be recovered. The inert matrix material should not give rise to new radioactive waste that needs to be safely disposed of as low or medium active waste [9].

Hydrometallurgical processes using solvent extraction technology are the industry standard for used light water reactor fuel reprocessing with the plutonium uranium reduction extraction (PUREX) process as the basis for all current commercial scale reprocessing plants. It consists of the initial dissolution of fuel into nitric acid and the consecutive separation. The fuel is dissolved in hot concentrated HNO_3. This step, which takes a few hours, dissolves the uranium, plutonium, and fission products, leaving the undissolved cladding to be disposed of as high active solid waste. A solution of 30% tri-*n*-butylphosphate (TBP) in kerosene type diluent is used initially to separate U and Pu from the vast majority of the fission products [10].

In order to achieve a significant reduction in long-term radiotoxicity of the high active waste, Am and Cm must also be separated from the PUREX raffinate, which is currently vitrified for subsequent disposal in deep geological repositories. The processes that have been developed over the past 20 years, are mainly based on the co-extraction of trivalent actinides and lanthanides and their subsequent separation [2, 11]. The separation of An(III) + Ln(III) from PUREX raffinate in a process called DIAMEX (diamide extraction) was proposed in the 1980s [12]. *N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide (DMDOHEMA) has become the reference molecule for the DIAMEX processs [13, 14] enhancing the extractive properties towards trivalent elements and shortening the degradation compounds formed by acidic hydrolysis and radiolysis [15]. Recently, a new process for recovery of trivalent actinides from PUREX-type raffinate utilizing *N,N,N',N'*-tetraoctyldiglycolamide (TODGA) was developed [16–22]. In a first step a very efficient extraction of An(III) and Ln(III) from acidic medium is performed, followed by their stripping using diluted nitric acid [19].

In this paper the reprocessability of magnesia and molybdenum based IMF is under investigation. This includes a brief investigation of their dissolution behavior at different acid concentrations (1–7 mol/L) and temperatures (room temperature and 90°C), although the main focus is on extraction. The extractability of Mg and Mo as well as the influence of macro amounts of matrix material on the extraction of U(VI), Eu(III), and Am(III) were examined. Extraction studies with TBP were performed under PUREX conditions. The two well-known DIAMEX type extractants DMDOHEMA and TODGA were studied for actinide(III) and lanthanide(III) extraction.

Experimental

Pellet fabrication

To investigate the reprocessability of molybdenum and magnesia based inert matrix fuels reference samples have been prepared. The pellets were characterized by means of density measurements, scanning electron microscope (SEM) investigation, and X-ray diffraction (XRD).

Magnesium oxide powder (Merck, pro analysis) was calcined at 600°C for 2 h and then milled by hand. The powder (500 mg) was compacted into cylindrical pellets with 10 mm diameter by cold uniaxial pressing. All MgO pellets were sintered for 5 h in air atmosphere at 1600°C. The density, determined by a geometrical method, of the MgO pellets used for dissolution experiments was 96 ± 3% TD (quotient of the theoretical density in percent).

Molybdenum pellets (10 mm diameter) were fabricated by compacting 1 g Mo powder (Strem Chemicals, 99.9%) at a pressure of 640 MPa using a cold uniaxial press. The pellets were then sintered at 1600°C for 5 h in argon atmosphere. The density of all pellets was measured by the geometrical method and was 92 ± 1% TD.

Dissolution experiments

The influence of temperature and nitric acid concentration on the dissolution of MgO and Mo pellets was investigated. Dissolution experiments were conducted in a two-necked round-bottom flask equipped with a Liebig condenser. During dissolution, the liquor was stirred using a magnetic stirring bar. An oil bath was used for temperature control. Nitric acid (Merck, pro analysis) was used for all dissolution experiments. If not stated otherwise 20 mL of acid were provided in the flask per 1 g of pellet (MgO, Mo) for each dissolution experiment, the stirring rate was set to 300 rpm, and the temperature was adjusted, then the pellet was added. During the dissolution process 50 μL samples were taken and measured in a calibration range of 0.1 to 100 μg/L with appropriate dilution of the analyte in 1% v/v HNO_3 (suprapure) solution. Molybdenum samples were centrifuged prior to dilution; for magnesium samples filtration and centrifugation was proven to be unnecessary. The inductively coupled plasma mass spectroscopy (ICP-MS) measurements were realized with the Elan 6100 DRC apparatus, developed by PerkinElmer and SCIEX.

Extraction experiments

The extraction of Mo, Mg, U, Am, and Eu by three different solvents was tested. The used solvents were:
- 30% TBP in TPH (hydrogenated tetrapropene, industrial kerosene diluent), PUREX solvent;
- 0.6 mol/L DMDOHEMA in Exxsol-d80 (industrial kerosene diluent), DIAMEX solvent;
- 0.2 mol/L TODGA in Exxsol-d80 (industrial kerosene diluent), DIAMEX-like solvent.

Equal volumes of 500 μL per phase were used in liquid-liquid extraction experiments. Aqueous solutions were spiked with trace amounts of [nat]U, [241]Am and [152]Eu, respectively.

Table 1. Magnesium solutions used for solvent extraction studies

Mg concentration [g/L]	Acidity [mol/L]	$c(NO_3^-)$ [mol/L]
0.008	2.89	3.09
0.081	2.84	3.09
0.784	2.67	3.09
7.85	2.37	3.09
23.6	1.23	3.09
37.5	0.01	3.09

Magnesium solutions (0.008–37.5 g/L) were prepared by dissolving a weighted amount of MgO in 3.09 mol/L HNO_3. Accordingly, the acid concentration decreased with increasing Mg concentration, due to partial neutralization of HNO_3 (compare Eq. (1)), while the nitrate concentration was constant. An overview of the Mg concentrations and the corresponding acid and nitrate concentrations of aqueous solutions used for the extraction experiments is shown in Table 1. The acid concentration of aqueous solutions was determined by potentiometric titration with a '798 MPT Titrino' from Metrohm. Titrations were carried out with 0.01 molar NaOH solutions.

Increasing weighted amounts of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ were dissolved in 3.09 mol/L HNO_3 for preparation of Mo solutions, keeping the nitrate concentration constant. The acid concentrations were determined by potentiometric titration, as described above, although simple measurement of the H^+ concentration might not be sufficient to describe the extremely complex acido-basic Mo(VI) chemistry. An overview of the Mo concentrations and the corresponding acid and nitrate concentrations is shown in Table 2.

The batch extraction experiments were performed in 2 mL glass vials in a thermostatted aluminum block at 22°C and the extraction time was 15 min.

The radioisotopes [241]Am and [152]Eu were directly analyzed using a high-purity germanium spectrometer system (EG&G Ortec, Munich, Germany; equipped with the Gamma Vision software) without any additional sample preparation. The γ-lines at 59.5 keV and 121.8 keV were examined for intensities of [241]Am and [152]Eu, respectively. The results are reported as distribution ratios D (D = $[M_{org}]/[M_{aq}]$), which have an uncertainty of ±5%, detection limits are 500 > D > 0.002.

Mg, Mo, and U were analyzed using ICP-MS to determine the concentration of each element in the organic and aqueous phase. The aqueous phases

Table 2. Overview of the Mo concentrations and the corresponding acid and nitrate concentrations

Mo concentration [g/L]	Acidity [mol/L]	$c(NO_3^-)$ [mol/L]
0.010	3.09	3.09
0.102	3.09	3.09
1.02	3.08	3.09
9.57	3.02	3.09
43.4	2.74	3.09
106.2	2.23	3.09

were diluted with 1% HNO_3 (suprapure) to an appropriate concentration and measured directly. The organic phases were diluted with 1% HNO_3 (suprapure) containing 0.2% Triton-X 100 in order to disperse the organic phase in the sample homogenously. The results are given as distribution ratios D.

Results and discussion

Dissolution behavior

In preparation for the well-established PUREX process spent fuel is dissolved in near boiling 7–10 mol/L nitric acid [10, 23]. Therefore, the dissolution behavior of MgO and Mo based inert matrix fuel was investigated in the heat (90°C). However, PuO_2 is expected to partially dissolve in concentrated nitric acid at elevated temperatures, but potentially less at mild conditions (room temperature, dilute nitric acid). The dissolution of plutonium from fresh and spent PuO_2 or MOX is complex and depends on synthesis, microstructure, and thermal as well as irradiation history [24–26]. The aim of this work is to evaluate conditions at which the matrix material can be selectively dissolved without dissolving high amounts of PuO_2. Therefore, dissolution behavior at mild conditions is also investigated. If the matrix material could be selectively dissolved and separated in a first dissolution step at mild conditions, the PuO_2 would then be dissolved in an additional step utilizing, e.g. boiling concentrated HNO_3 and Ag(II) or Ce(IV) as catalysts [24–26].

The dissolution of MgO may be described by the following equation [27]:

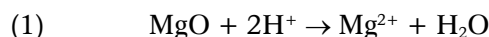$$(1) \qquad MgO + 2H^+ \rightarrow Mg^{2+} + H_2O$$

Figure 1 displays the dissolution kinetics of ceramic MgO pellets at 90°C (open symbols) and at room temperature (filled symbols) in initially 2.5 and 7 mol/L HNO_3. The intermediate acid concentrations were also examined, but are not shown here for reasons of clarity. In the heat MgO pellets quantitatively dissolved within about one hour. The acid concentration has barely any effect on the rate of dissolution of MgO in the range of 2.5 to 7 mol/L, but the rate of dissolution is strongly dependent on the temperature. Complete dissolution of a MgO pellet in nitric acid at room temperature is achieved within one day. The temperature dependence of dissolution rates is typically expressed using Arrhenius law:

$$(2) \qquad k = Ae^{-E/RT}$$

with the pre-exponential factor A, the activation energy E, the rate constant k, the gas constant R and the temperature T. The activation energies for the different acid concentrations were calculated from the slopes of the linear fits (not shown here). The obtained activation energies for dissolution of magnesia in nitric acid of different concentration show no clear trend but vary in the range from 40 to 60 kJ/mol, which indicates a surface controlled dissolution [28].
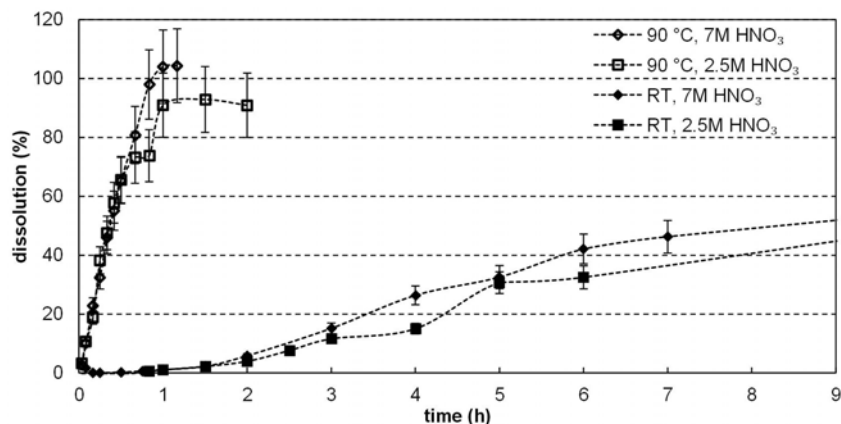
Fig. 1. Dissolution of MgO pellets in 2.5 and 7 mol/L HNO₃ at room temperature (filled symbols) and 90°C (open symbols).

The surface or microstructure plays a key role in dissolution [29, 30] and hence, the dissolution rate is usually normalized to the reactive surface area to allow comparability with other samples with different microstructure or geometry. However, well--established methods such as BET (Brunauer-Emmet-Teller) cannot be applied to pellets. A possibility to get a better evaluation of the pellet surface would be with a method based on SEM observation as described by Horlait *et al*. [31], but this is beyond the scope of this paper. However, it should be briefly mentioned that several indications were found for a surface controlled dissolution. For instance, we observed a heterogeneous surface development during dissolution, which can probably be attributed to heterogeneous crystal orientations. This is in agreement with the observation by Suárez and Compton [32] within an atomic force microscopy study, that the different surfaces of the MgO crystal (100), (110), and (111) dissolve in hydrochloric acid via heterogeneous etch patterns.

The dissolution of molybdenum is an oxidative process which may be described by the following equation:

$$(3) \quad Mo + 2HNO_3 \rightarrow MoO_3 + 2NO + H_2O$$
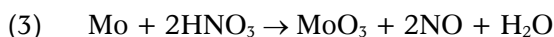
However, the produced MoO₃ does not readily dissolve in nitric acid [33]. The aqueous chemistry of molybdenum is quite complex. The speciation of molybdenum has been studied intensively in hydrochloric and perchloric acid medium, but little is known about the speciation in nitric acid medium, especially at high acidities, which are relevant for the dissolution of IMF. Molybdenum(VI) is well known to exist as molybdate in alkaline solutions of pH > 7. With an increase in the molybdenum concentration molybdate ions polymerize to form isopolymolybdates, which have been reported to exist in the region of molybdenum concentrations >10⁻⁴ mol/L. Below this concentration, acidification of the molybdate proceeds to form monoprotonated, diprotonated and finally cationic species. Cationic species exist in the region of pH below one. In the acidic region, the existence of dimeric cations has been suggested in the more concentrated solutions of molybdenum [34]. The speciation of molybdenum during dissolution of molybdenum pellets was studied by electrospray ionization mass spectrometry (ESI-MS), but is beyond the scope of this paper and will be published elsewhere.

The typical dissolution kinetics of metallic Mo pellets at 90°C (open symbols) and at room temperature (filled symbols) in 1 and 7 mol/L HNO₃ is depicted in Fig. 2. Unlike MgO, the dissolution behavior of molybdenum in nitric acid strongly depends on the acid concentration; the rate of dissolution velocity in 7 mol/L HNO₃ was significantly higher than in 1 mol/L HNO₃. However, during dissolution of a Mo pellet in 7 mol/L nitric acid at 90°C a huge
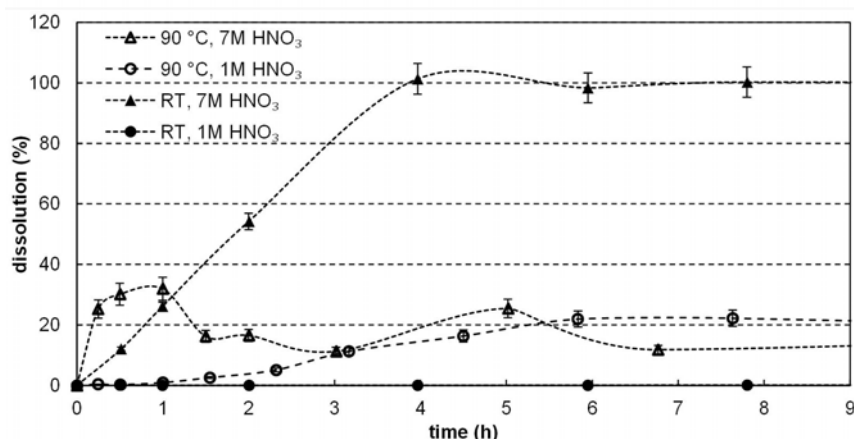

Fig. 2. Dissolution of Mo pellets in 1 and 7 mol/L HNO₃ at room temperature (filled symbols) and 90°C (open symbols).
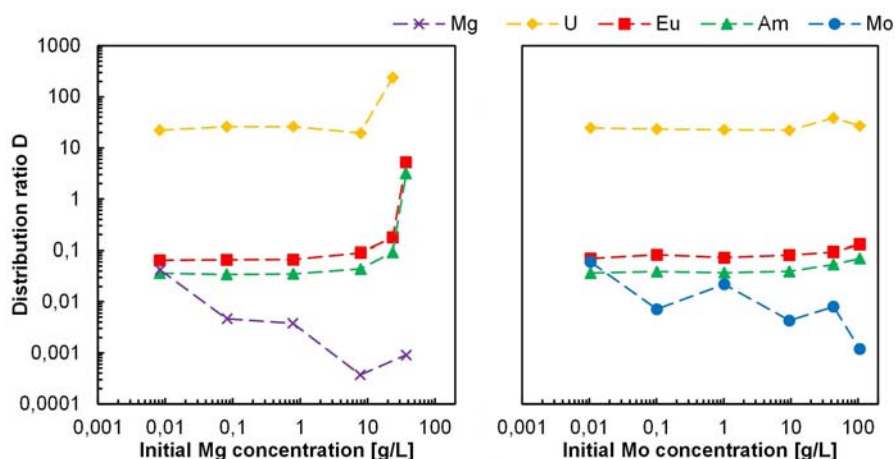
Fig. 3. Distribution ratios of Mg(II), Eu(III), Am(III), U(VI), and Mo(VI) using TBP in the organic phase and nitric acid solutions with increasing Mg or Mo concentrations in the aqueous phase. Organic phase: 30% TBP in TPH, Aqueous phase: (left) increasing amount of Mg (8–38 g/L) in initially 3 mol/L HNO_3, (right) increasing amount of Mo (10–90 g/L) in initially 3 mol/L HNO_3.

amount of precipitation occurred within the first 30 min of the dissolution. The molybdenum concentration in the solution increased during the initial phase of the dissolution. However, it then decreased due to the onset of the precipitation and did not exceed 20% of the expected amount. The dissolution of Mo at room temperature is expected to proceed with significantly less precipitation. Compared to the dissolution at 90°C, only a very low amount of precipitation occurred instantly at room temperature. Precipitates formed at all investigated conditions and were identified as MoO_3 (molybdite) by XRD. X-ray diffraction analyses were performed in the range from 10 to 100° 2θ at room temperature with the D8 Advance (θ–2θ geometry) and the D4 Endeavor (θ-θ geometry) from Bruker AXS GmbH. All precipitates were hand milled prior to analysis. However, only about 5% of the molybdenum precipitated in 1 molar nitric acid at room temperature, while about 80% precipitated in 7 mol/L HNO_3 in the heat.

Both molybdenum and magnesia can be dissolved at mild conditions although the dissolution is faster at elevated temperatures. However, a quantitative separation will not be achieved during dissolution and needs to be accomplished in a subsequent separation step.

Extraction

First, the extractability of Mg^{2+} and Mo^{6+} was investigated by the PUREX solvent 30% TBP in TPH. Additionally, the influence of increasing Mg and Mo concentration on uranium, americium and europium extraction was studied. For this purpose the solutions were spiked with trace amounts of ^{nat}U, ^{241}Am and ^{152}Eu, although Mo(VI) is a proven complexing agent for U(VI) [35].

With the PUREX solvent Mg was not extracted (D < 0.1). Uranium was well extracted with distribution ratios of ~25 (Fig. 3, left). Americium and europium were poorly extracted with D < 0.1, although at the highest initial Mg concentration an increase in the Am/Eu distribution ratios was observed. This

was caused by the decreasing acid concentration as shown in Table 1 for the Mg system and Table 2 for the Mo system, while the nitrate concentration was constant. It is well known that TBP extracts also nitric acid at high acidity by solvation mechanism. Thus at low acitity the free TBP concentration in the organic phase is higher, resulting in increased uranium, americium and europium distribution ratios. Molybdenum was also not extracted (D < 0.1). Uranium was well extracted in the presence of molybdenum with distribution ratios of ~22 (Fig. 3, right). Americium and europium were poorly extracted with D ratios ~0.1. No third phase formation nor precipitation was observed in both cases.

Magnesium as well as molybdenum were not extracted by the PUREX solvent 30% TBP in TPH, but remained in the aqueous phase together with the lanthanides and minor actinides. Therefore, the extractability of MgO and Mo by DIAMEX type solvents as well as their influence on the extraction of actinides and lanthanides is explored in the next step.

With the DIAMEX solvent, a fine precipitation was observed at c_{ini}(Mg) = 38 g/L. Magnesium was not extracted with D ~ 0.01 at the lower initial Mg concentrations. However, an increasing extraction of Mg was observed at the highest initial Mg concentrations. The increasing extraction of Mg with DMDOHEMA was surprising and needs to be further investigated. However, the behavior of the actinides (U, Am) and Eu is in line with literature data. Uranium was very well extracted (D ~ 100), and Am (D ~ 5) and Eu (D ~ 3) were well extracted (Fig. 4, left). Third phase formation was also observed in the Mo system at c_{ini}(Mo) = 43 g/L and a precipitation occurred at c_{ini}(Mo) = 90 g/L. This was due to the good extraction of Mo by DMDOHEMA, with D reaching a maximum of 4 (Fig. 4, right). Uranium was very well extracted (D > 100), and Am (D ~ 4) and Eu (D ~ 2) were well extracted.

In the presence of macro amounts Mg, no third phase formation or precipitation was observed with TODGA. Magnesium was not extracted, with D ~ 0.01. Uranium was well extracted with D ~ 10 and Am and Eu were very well extracted with D
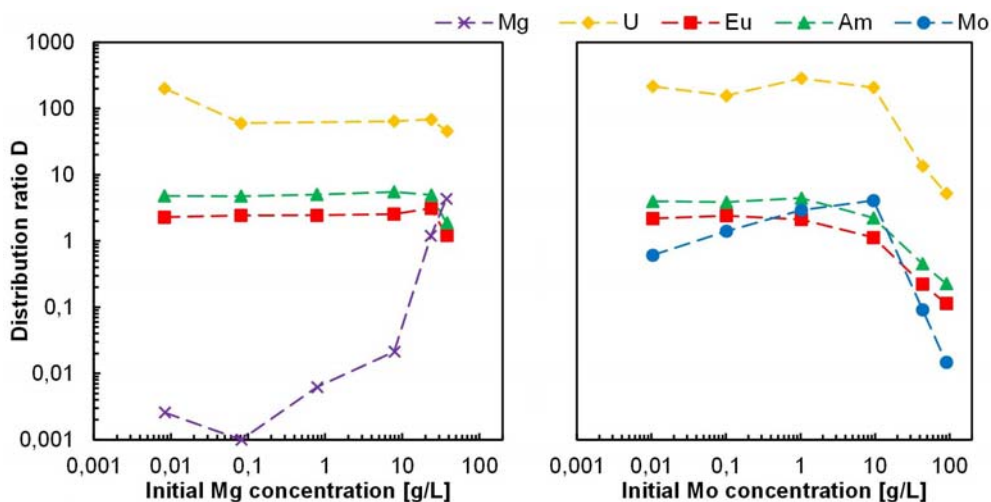
Fig. 4. Distribution ratios of Mg(II), Eu(III), Am(III), U(VI), and Mo(VI) using DMDOHEMA in the organic phase and nitric acid solutions with increasing Mg or Mo concentrations in the aqueous phase. Organic phase: 0.6 mol/L DMDOHEMA in Exxsol-d80. Aqueous phase: (left) increasing amount of Mg (8–38 g/L) in initially 3 mol/L HNO_3, (right) increasing amount of Mo (10–90 g/L) in initially 3 mol/L HNO_3.

> 100 (Fig. 5, left). In the case of molybdenum a fine precipitate was observed at $c_{ini}(Mo) = 90$ g/L. Molybdenum was moderately extracted with D of 2.5 at low initial Mo concentration, while decreasing Mo distribution ratios are observed at higher Mo concentrations (Fig. 5, right). Uranium was well extracted with D ~ 10 and Am and Eu were very well extracted with D > 100.

The extraction results show that Mo is partly extracted by DMDOHEMA and TODGA, causing third phase formation or precipitation problems at the highest initial Mo-concentrations. The behavior of the actinides (U, Am) and Eu is in line with literature data [36–39].

Conclusions and outlook

The dissolution of MgO is possible even under relatively mild conditions (2.5 mol/L HNO_3, room

temperature). Magnesium oxide could be separated in a first dissolution step at mild conditions, while the actinides would be dissolved in an additional step utilizing, e.g. boiling concentrated HNO_3.

The rate of dissolution of Mo was strongly dependent on the acid concentration as well as the temperature. The dissolution of Mo pellets in HNO_3 was complex. It was accompanied by precipitation, especially at high acid concentrations and temperatures. Further dissolution optimization studies are planned in the near future in glove boxes (fresh PuO_2 + Mo matrix pellets).

The matrix elements Mg and Mo were not extracted using the PUREX solvent. In the DIAMEX solvent Mg was extracted at low acidity, while Mo was extracted with moderate distribution ratios. The TODGA solvent was not able to extract Mg, but Mo was slightly extracted at low Mo concentrations. However, both the DMDOHEMA and the TODGA system suffer from third phase formation and pre-
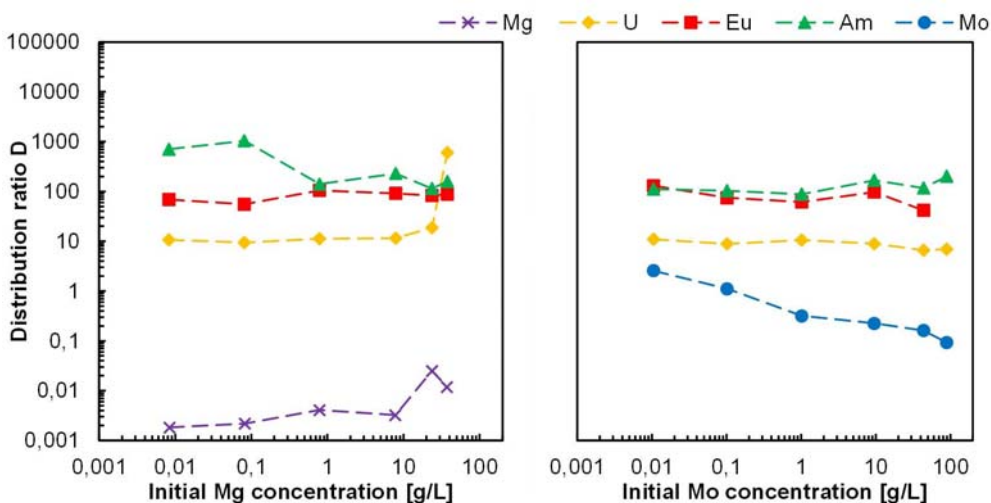

Fig. 5. Distribution ratios of Mg(II), Eu(III), Am(III), U(VI), and Mo(VI) using TODGA in the organic phase and nitric acid solutions with increasing Mg or Mo concentrations in the aqueous phase. Organic phase: 0.2 mol/L TODGA in Exxsol-d80. Aqueous phase: (left) increasing amount of Mg (8–38 g/L) in initially 3 mol/L HNO_3, (right) increasing amount of Mo (10–90 g/L) in initially 3 mol/L HNO_3.

cipitation issues, which will have to be resolved. However, methods have to be developed to separate Mg and Mo to improve the final conditioning of the remaining fission products before vitrification.

References

1. Pillon, S. (2012). Actinide-bearing fuels and transmutation targets. In R. J. M. Konings (Ed.), *Comprehensive nuclear materials* (Vol. 3, pp. 109–141). Oxford: Elsevier.
2. Modolo, G., Wilden, A., Geist, A., Magnusson, D., & Malmbeck, R. (2012). A review of the demonstration of innovative solvent extraction processes for the recovery of trivalent minor actinides from PUREX raffinate. *Radiochim. Acta*, *100*, 715–725. DOI: 10.1524/ract.2012.1962.
3. Montel, J. -M. (2011). Minerals and design of new waste forms for conditioning nuclear waste. *C. R. Geosci.*, *343*, 230–236. DOI: 10.1016/j.crte.2010.11.006.
4. Lamontagne, J., Béjaoui, S., Hanifi, K., Valot, C., & Loubet, L. (2011). Swelling under irradiation of MgO pellets containing americium oxide: The ECRIX-H irradiation experiment. *J. Nucl. Mater.*, *413*, 137–144. DOI: 10.1016/j.jnucmat.2011.04.013.
5. D'Agata, E., Klaassen, F., Sciolla, C., Fernandes-Carretero, A., & Bonnerot, J. M. (2009). Helios: The new design of the irradiation of U-free fuels for americium transmutation. In Proceedings of the Global, 6–11 September 2009 (pp. 2006–2015). Paris, France.
6. Delage, F., Belin, R., Chen, X. -N., D'Agata, E., Klaassen, F., Knol, S., Maschek, W., Ottaviani, J. P., Rineiski, A., Sobolev, V., Somers, J., Staicu, D., Thetford, R., Wallenius, J., & Wernli, B. (2010). Minor actinide transmutation in an accelerator-driven system prototype: Results from fuel developments within the European programme EUROTRANS. In Proceedings of the Actinide and Fission Product Partitioning and Transmutation – Eleventh Information Exchange Meeting, 1–4 November 2010 (pp. 177–186). San Francisco.
7. Haas, D., Fernandez, A., Staicu, D., Somers, J., Maschek, W., Liu, P., & Chen, X. (2008). CERMET fuel behavior and properties in ADS reactors. *Energy Conv. Manag.*, *49*, 1928–1933. DOI: 10.1016/j.enconman.2007.12.027.
8. Ekberg, C., deVisser-Tynova, E., Retegan, T., Sarsfield, M., & Wallenius, J. (2014). ASGARD. In Proceedings of the Sustainable Nuclear Energy Conference SNEC, 9–11 April 2014. Manchester.
9. Ouvrier, N., & Boussier, H. (2012). Recycling of MgO, Mo & ZrO$_2$ based actinide-bearing matrices: Assessment of reprocessing feasibility & waste production. *Procedia Chem.*, *7*, 322–327. DOI: 10.1016/j.proche.2012.10.051.
10. Loveland, W. D., Morrissey, D. J., & Seaborg, G. T. (2006). *Modern nuclear chemistry*. New York, NY: Wiley.
11. Taylor, R., Bourg, S., Glatz, J. -P., Modolo, G. (2015). Developement of actinide separation processes for future nuclear fuel cycles in Europe. *Nucl. Future*, *11*(4), 38–43.
12. Courson, O., Lebrun, M., Malmbeck, R., Pagliosa, G., Romer, K., Satmark, B., & Glatz, J. -P. (2000). Partitioning of minor actinides from HLLW using the DIAMEX process. Part 1 – Demonstration of extraction performances and hydraulic behaviour of the solvent in a continuous process. *Radiochim. Acta*, *88*, 857–863. DOI: 10.1524/ract.2000.88.12.857.
13. Serrano-Purroy, D., Christiansen, B., Glatz, J. -P., Malmbeck, R., & Modolo, G. (2005). Towards a DIAMEX process using high active concentrate. Production of genuine solutions. *Radiochim. Acta*, *93*, 357–361. DOI: 10.1524/ract.93.6.357.65645.
14. Serrano-Purroy, D., Baron, P., Christiansen, B., Malmbeck, R., Sorel, C., & Glatz, J. -P. (2005). Recovery of minor actinides from HLLW using the DIAMEX process. *Radiochim. Acta*, *93*, 351–355. DOI: 10.1524/ract.93.6.351.65642.
15. Baron, P., Hérès, X., Lecomte, M., & Masson, M. (2001). Separation of the minor actinides: the DIAMEX-SANEX concept. In Proceedings of the International Conference on Future Nuclear Systems, GLOBAL'01, 9–13 September 2001. Paris, France.
16. Sasaki, Y., & Choppin, G. R. (1996). Solvent extraction of Eu, Th, U, Np and Am with N,N'-dimethyl-N,N'-dihexyl-3-oxapentanediamide and its analogous compounds. *Anal. Sci.*, *12*, 225–230. DOI: 10.2116/analsci.12.225.
17. Sasaki, Y., & Choppin, G. R. (1998). Extraction of Np(V) by N,N'-dimethyl-N,N'-dihexyl-3-oxapentane-diamide. *Radiochim. Acta*, *80*, 85–88. DOI: 10.1524/ract.1998.80.2.85.
18. Sasaki, Y., Sugo, Y., Suzuki, S., & Tachimori, S. (2001). The novel extractants, diglycolamides, for the extraction of lanthanides and actinides in HNO$_3$-*n*-dodecane system. *Solvent Extr. Ion Exch.*, *19*, 91–103. DOI: 10.1081/sei-100001376.
19. Modolo, G., Vijgen, H., Schreinemachers, C., Baron, P., & Dinh, B. (2003). TODGA process developement for partitioning of actinides(III) from PUREX raffinate. In Proceedings of the GLOBAL, 16–20 November 2003 (pp. 1926–1930). New Orleans, Louisiana, USA.
20. Geist, A., & Modolo, G. (2009). TODGA process development: an improved solvent formulation. In Proceedings of the GLOBAL (The Nuclear Fuel Cycle: Sustainable Options & Industrial Perspectives), 6–11 September 2009 (pp. 1022–1026, paper 9193). Paris, France.
21. Modolo, G., Asp, H., Schreinemachers, C., & Vijgen, H. (2007). Development of a TODGA based process for partitioning of actinides from a PUREX raffinate Part I: Batch extraction optimization studies and stability tests. *Solvent Extr. Ion Exch.*, *25*, 703–721. DOI: 10.1080/07366290701634578.
22. Magnusson, D., Christiansen, B., Glatz, J. P., Malmbeck, R., Modolo, G., Serrano-Purroy, D., & Sorel, C. (2009). Demonstration of a TODGA based extraction process for the partitioning of minor actinides from a PUREX raffinate. *Solvent Extr. Ion Exch.*, *27*, 26–35, DOI: 10.1080/07366290802544726.
23. Fukasawa, T., & Ozawa, Y. (1986). Relationship between dissolution rate of uranium dioxide pellets in nitric acid solutions and their porosity. *J. Radioanal. Nucl. Chem. Lett.*, *106*, 345–356. DOI: 10.1007/BF02163667.
24. Ryan, J. L., Bray, L. A., Wheelwright, E. J., & Bryan, G. H. (1990). *Catalyzed electrolytic plutonium oxide dissolution (CEPOD): The past seventeen years and future potential*. United States: American Chemical Society.

25. Uriarte, A. L., & Rainey, R. H. (1965). *Dissolution of high-density UO₂, PuO₂, and UO₂-PuO₂ pellets in inorganic acids*. Commission, U.S.A.E., Oak Ridge, Tennessee: Oak Ridge National Laboratory. (ORNL-3695).

26. Inoue, A. (1988). Enhanced dissolution of PuO_2 in nitric acid using uranium(IV). *J. Chem. Soc. Faraday Trans.*, *84*, 1195–1197. DOI: 10.1039/F19888401195.

27. Fedorockova, A., & Raschman, P. (2008). Effects of pH and acid anions on the dissolution kinetics of MgO. *Chem. Eng. J.*, *143*, 265–272. DOI: 10.1016/j.cej.2008.04.029.

28. Jordan, G., & Rammensee, W. (1996). Dissolution rates and activation energy for dissolution of brucite (001): A new method based on the microtopography of crystal surfaces. *Geochim. Cosmochim. Acta*, *60*, 5055–5062. DOI: 10.1016/S0016-7037(96)00309-2.

29. Lüttge, A., Arvidson, R. S., & Fischer, C. (2013). A stochastic treatment of crystal dissolution kinetics. *Elements*, *9*, 183–188. DOI: 10.2113/gselements.9.3.183.

30. Finkeldei, S., Brandt, F., Rozov, K., Bukaemskiy, A. A., Neumeier, S., & Bosbach, D. (2014). Dissolution of ZrO_2 based pyrochlores in the acid pH range: A macroscopic and electron microscopy study. *Appl. Geochem.*, *49*, 31–41. DOI: 10.1016/j.apgeochem.2014.06.014.

31. Horlait, D., Claparede, L., Tocino, F., Clavier, N., Ravaux, J., Szenknect, S., Podor, R., & Dacheux, N. (2014). Environmental SEM monitoring of $Ce_{1-x}Ln_xO_{2-x/2}$ mixed-oxide microstructural evolution during dissolution. *J. Mater. Chem.*, *2*, 5193–5203, DOI: 10.1039/C3TA14623E.

32. Suárez, M. F., & Compton, R. G. (1998). Dissolution of magnesium oxide in aqueous acid: An atomic force microscopy study. *J. Phys. Chem. B*, *102*, 7156–7162. DOI: 10.1021/jp982260x.

33. Tytko, K. H. (1989). *Mo: Molybdenum. System number 53. Molybdenum oxide hydrates, oxomolybdenum species in aqueous solutions*. Berlin: Springer.

34. Fujii, T., Yamana, H., Watanabe, M., & Moriyama, H. (2001). Extraction of molybdenum from nitric acid by octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide. *Solvent Extr. Ion Exch.*, *19*, 127–141. DOI: 10.1081/sei-100001378.

35. Saito, A., & Choppin, G. R. (1998). Complexation of uranyl(VI) with polyoxometalates in aqueous solutions. *J. Alloys Compd.*, *271/273*, 751–755. DOI: 10.1016/S0925-8388(98)00200-X.

36. Suzuki, H., Sasaki, Y., Sugo, Y., Apichaibukol, A., & Kimura, T. (2004). Extraction and separation of Am(III) and Sr(II) by N,N,N',N'-tetraoctyl-3-oxa-pentanediamide (TODGA). *Radiochim. Acta*, *92*, 463–466. DOI: 10.1524/ract.92.8.463.39276.

37. Ansari, S. A., Pathak, P. N., Manchanda, V. K., Husain, M., Prasad, A. K., & Parmar, V. S. (2005). N,N,N',N'-Tetraoctyl diglycolamide (TODGA): a promising extractant for actinide partitioning from high-level waste (HLW). *Solvent Extr. Ion Exch.*, *23*, 463–479. DOI: 10.1081/sei-200066296.

38. Cuillerdier, C., Musikas, C., Hoel, P., Nigond, L., & Vitart, X. (1991). Malonamides as new extractants for nuclear waste solutions. *Separ. Sci. Technol.*, *26*, 1229–1244. DOI: 10.1080/01496399108050526.

39. Cuillerdier, C., Musikas, C., & Nigond, L. (1993). Diamides as actinide extractants for various waste treatments. *Separ. Sci. Technol.*, *28*, 155–175. DOI: 10.1080/01496399308019484.