Gamma radiolytic stability of CyMe₄BTBP and the effect of nitric acid

Holger Schmidt,
Andreas Wilden,
Giuseppe Modolo,
Jaroslav Švehla,
Bohumir Grüner,
Christian Ekberg

Abstract. The highly selective nitrogen donor ligand CyMe₄BTBP for An(III) separation by solvent extraction was irradiated in a ⁶⁰Co γ-source under varying conditions. Organic solutions of 10 mmol/L ligand in 1-octanol were contacted with different concentrations of nitric acid to observe the influence of an aqueous phase during irradiation. In subsequent liquid-liquid extraction experiments, distribution ratios of ²⁴¹Am and ¹⁵²Eu were determined. Distribution ratios decreased with increasing absorbed dose when irradiation was performed in the absence of nitric acid. With addition of nitric acid, initial distribution ratios remained constant over the whole examined dose range up to 300 kGy. For qualitative determination of radiolysis products, HPLC-MS measurements were performed. The protective effect of nitric acid was confirmed, since in samples irradiated with acid contact, no degradation products were observed, but only addition products of the 1-octanol molecule to the CyMe₄BTBP molecule.

Key words: CyMe₄BTBP • gamma radiolysis • liquid-liquid extraction • nitric acid • partitioning • protective effect

H. Schmidt, A. Wilden, G. Modolo[✉]
Institut für Energie- und Klimaforschung, Nukleare
Entsorgung und Reaktorsicherheit (IEK-6),
Forschungszentrum Jülich GmbH (FZJ),
52425 Jülich, Germany,
Tel.: +49 2461 61 4896, Fax: +49 2461 61 2450,
E-mail: g.modolo@fz-juelich.de

J. Švehla, B. Grüner
Institute of Inorganic Chemistry, Academy of Sciences
of the Czech Republic,
Hlavní 1001, 25068 Husinec-Rež, Czech Republic

C. Ekberg
Nuclear Chemistry & Industrial Materials Recycling,
Department of Chemical and Biochemical Engineering,
Chalmers University of Technology,
Kemigården 4, 41296 Gothenburg, Sweden

Received: 23 June 2015

Accepted: 15 September 2015

Introduction

Within international research in partitioning and transmutation (P&T), the separation of trivalent actinides (An(III)) from the chemical similar trivalent lanthanides (Ln(III)) is a main task that was comprehensively studied within the last two decades [1–3].

The investigated solvent extraction processes often follow the plutonium uranium reduction extraction (PUREX) process, in which uranium and plutonium are recycled from dissolved spent nuclear fuel solutions. For An(III) separation, a two-cycle concept, the so-called DIAMEX-SANEX concept, was developed [4]. In the first cycle the trivalent actinides were co-separated together with the lanthanides in the diamide extraction (DIAMEX) process [5, 6]. In the subsequent selective actinide extraction (SANEX) process, An(III) were selectively partitioned using the highly selective nitrogen donor ligand CyMe₄BTBP (6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)-[2,2']-bipyridine) (Fig. 1) [7, 8]. A hot SANEX process demonstration was conducted using a genuine feed solution containing Ln(III) as well as Am(III) and Cm(III). Those An(III) were selectively extracted, whereas the lanthanides were routed to the raffinate stream [9]. In further work this SANEX process was modified to be able to extract the actinides directly from PUREX raffinate [10–12].

CyMe₄BTBP

6,6'-Bis(5,5,8,8-tetramethyl-
5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)
[2,2']-bipyridine

Fig. 1. Chemical structure of the CyMe₄BTBP ligand.

For the development of processes on an industrial scale, one main issue to consider is the detailed knowledge of radiolytic stability of the chemicals used since a solvent would be in contact for longer times with highly radioactive process streams. Degradation of the solvent may lead to the production of interfering degradation products, decreases in ligand concentration and changes in solvent viscosity as well as phase separation parameters [13]. This degradation may result in losses in selectivity and affinity for target metal extraction.

Radiolytic degradation of the BTBP ligand family was investigated previously [14–16]. A variety of different BTBP molecules was developed, such as C5-BTBP (6,6'-bis(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2']bipyridine) or the annulated MF2-BTBP (4-tert-butyl-6,6'-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2']-bipyridine) and tested for their process performance [17]. Since it was proven that annulated BTBPs are much more stable towards radiolytic degradation than the tetra alkyl substituted BTBPs, those annulated systems were further investigated. Finally, the CyMe₄BTBP system was chosen as reference system in European research, resulting in the above mentioned SANEX process. Radiolytic stability of the SANEX solvent (CyMe₄BTBP + DMDOHEMA (*N,N'*-dimethyl-*N,N'*-dioctylhexylethoxymalonamide) in octanol) was studied by Magnusson *et al.* [18]. They investigated the radiolytic degradation for alpha as well as gamma radiation depending on the absorbed dose. The degradation of the extractant was found to be more severe for gamma radiolysis, as the reduction of distribution ratios was 40% higher compared to alpha radiolysis. This was explained by the higher LET of alpha radiation yielding in denser radiation tracks, allowing much faster recombination of radicals formed than in the case of gamma radiation [18].

The presence of an aqueous phase during irradiation of C5-BTBP in cyclohexanone was studied by Fermvik *et al.* [19]. It was found that in the presence of an aqueous phase the degradation of the extractant increased. A general review of the radiation chemistry of selective ligands for trivalent actinide recovery was published by Mincher *et al.* [20]. Su-

lich *et al.* examined the radiolysis of CyMe₄BTBP in 1-octanol pre-equilibrated with nitric acid using electron pulse radiolysis [21]. They added benzophenone and observed a protective effect on the ligand which was attributed to the addition of the aromatic ketone in higher concentration than the ligand, preferentially reacting with solvated electrons.

In this work, the radiolytic degradation of CyMe₄BTBP in 1-octanol and the influence of an aqueous phase in contact during irradiation were investigated. Experiments were conducted without an aqueous phase as well as in contact to different diluted nitric acid solutions.

Experimental part

CyMe₄BTBP was purchased from Technocomm Ltd., Falkland, United Kingdom with a purity >98%. 1-Octanol (analytical grade, >99%) and concentrated nitric acid (65%, analytical grade) were purchased from Merck, Darmstadt, Germany.

Radiolysis experiments

Solutions of CyMe₄BTBP in 1-octanol (10 mmol/L) were irradiated either without contact to an aqueous phase or in contact to different diluted nitric acid solutions (0.1, 1.0 and 4.0 mol/L HNO₃). The irradiation was performed at the Department of Chemical and Biochemical Engineering at the Chalmers University of Technology in Gothenburg, Sweden. A ⁶⁰Co γ-source (Gammacell 220, Atomic Energy of Canada Ltd.) with a dose rate of ~9.5 kGy/h was used and samples were irradiated up to absorbed doses of 300 kGy. With increasing absorbed dose, the color of the former light yellow organic phase turned into a more reddish/orange color, which could indicate degradation of the pyridine moieties.

Liquid-liquid extraction

After removing the irradiated samples from the Gammacell, phases were separated (if necessary) and batch shaking experiments were performed. In each experiment 500 μL of the irradiated organic phase were contacted with 500 μL fresh 1.0 mol/L HNO₃ which was spiked with an ²⁴¹Am (1.6 kBq) and a ¹⁵²Eu (2.8 kBq) tracer. The samples were vigorously mixed for 90 min in a shaking device (2500 rpm) at 22°C and after centrifugation the phases were separated and aliquots of each phase were taken for analysis. Gamma spectroscopy was performed with a high-purity germanium detector obtained from EG&G Ortec, Munich, Germany and equipped with the Gamma Vision software. The gamma lines at 59.5 keV and 121.8 keV were analyzed for ²⁴¹Am and ¹⁵²Eu, respectively. The results are reported as distribution ratios *D* ($D = [M_{org}]/[M_{aq}]$), which have an uncertainty of ±5%, and where detection limits are $500 > D > 0.002$.

HPLC-MS experiments

MS measurements were performed using a Finnigan LCQ Fleet™ spherical Ion Trap LC/MS_n instrument (Thermo Scientific). All mass spectra were measured with APCI interface. 25 µL of the samples of initial concentration of the ligand were diluted to a volume of 1.0 mL with acetonitrile (for LC-MS, Aldrich, gradient grade). Mass spectra from direct infusion by a syringe were measured with APCI in positive mode. Conditions used for APCI interface: flow rate from a syringe infusion pump: 10 µL/min; sheath gas flow 15 L/min; auxiliary gas flow at 7 L/min, source voltage: 3.75 kV, vaporizer temperature 400°C; capillary temperature 250°C; capillary voltage 48 V, tube lens voltage 100 V and mass range from 50 to 2000.

Results and discussion

The radiolytic stability of CyMe₄BTBP was first studied in the liquid-liquid extraction experiments using solvents irradiated to different doses up to 300 kGy. The irradiated samples were then analyzed by high-pressure liquid chromatography mass spectrometry (HPLC-MS) to determine the radiolysis products.

Liquid-liquid extraction experiments

Figure 2 shows the distribution ratios of ²⁴¹Am and ¹⁵²Eu as a function of absorbed dose for initially 10 mmol/L CyMe₄BTBP in 1-octanol, when the organic phase was irradiated without contact to an aqueous phase. Both, the americium and europium distribution ratios decreased with increasing absorbed dose, in line with observations from Magnusson *et al.* [18] who used a mixture of CyMe₄BTBP + DMDOHMA in octanol. Decreasing distribution ratios were observed up to an absorbed dose of

Fig. 2. ²⁴¹Am and ¹⁵²Eu distribution ratios of CyMe₄BTBP irradiated without contact to an aqueous phase (closed symbols) and in contact with 0.1 mol/L nitric acid (open symbols) as a function of the absorbed dose. Organic phase: initially 0.01 mol/L ligand in 1-octanol, irradiated by ⁶⁰Co γ radiation, dose rate ~9.5 kGy/h. Aqueous phase: fresh 1 mol/L HNO₃, spiked with ²⁴¹Am and ¹⁵²Eu tracer; 90 min shaking time, 22°C.

200 kGy (europium: 100 kGy), where the detection limit was reached. A linear decrease in distribution ratios was observed for europium (circles). For americium (squares), a delayed decrease in distribution ratios was found. After 75 kGy absorbed dose the slope of decreasing distribution ratios became steeper.

This could be explained by the formation of an intermediate species (see HPLC-MS section) that is also able to extract Am(III) to a certain amount, but is prone to radiolytic degradation with increasing dose itself. This behavior suggests there is no direct and exclusive degradation of the ligand by direct gamma irradiation alone but predominantly through indirect radiolysis [22–24]. It is well known, that during irradiation reactive radicals are formed mainly by radiolysis of the diluent, which can react with the extractant molecules (see discussion HPLC-MS, Eqs. (1)–(4)). Diluent molecules are present in much higher concentration than extractant molecules and are therefore more available for direct radiolysis.

The effect of nitric acid during irradiation was studied. Therefore, the organic solvent was irradiated in contact with different nitric acid concentrations from 0.1 to 4.0 mol/L HNO₃. For diluted 0.1 mol/L nitric acid, we could observe just slightly increased distribution ratios (Fig. 2). Irradiation experiments performed in contact with 1.0 mol/L nitric acid resulted in much higher distribution ratios. The observed distribution ratios did not decrease with increasing dose and the Am(III)/Eu(III) separation factor ($SF_{M1/M2} = D_{M1}/D_{M2}$) remained at the initial level with no observable changes (Fig. 3).

Obviously, the extracting system was protected by nitric acid against gamma radiation. The protection mechanism still needs to be resolved and in future experiments the individual influences of nitrate, acidity and water content will be studied. However, the added nitric acid seems to scavenge radicals built during radiolysis of the diluent. With increasing concentration of nitric acid from 0.1 mol/L to 1.0 mol/L, this scavenging became more effective until no reduction of distribution ratios was observed even at the highest doses studied here (300 kGy). Increase of the nitric acid concentration to 4.0 mol/L during irradiation

Fig. 3. ²⁴¹Am and ¹⁵²Eu distribution ratios of CyMe₄BTBP irradiated in contact with 1.0 mol/L nitric acid as a function of the absorbed dose. Organic phase: initially 0.01 mol/L ligand in 1-octanol, irradiated by ⁶⁰Co γ radiation, dose rate ~9.5 kGy/h. Aqueous phase: fresh 1 mol/L HNO₃, spiked with ²⁴¹Am and ¹⁵²Eu tracer; 90 min shaking time, 22°C.

showed no further improvement. For clarification of the radiolysis mechanism HPLC-MS measurements were conducted to identify the radiolysis products and to investigate the influence of nitric acid addition on the radiolysis mechanism.

HPLC-MS analysis

Qualitative HPLC-MS analysis was performed to identify the radiolysis products of the gamma irradiated ligand solutions. Results of the liquid-liquid extraction studies suggest that there is at least one new species formed during irradiation in contact with nitric acid that is also able to extract the actinides. In neat samples (no irradiation, no contact to nitric acid, but prepared at the same time as the samples for irradiation) only the molecule peak was found $m/z = (M + H^+) = 535.4$ u. When irradiating the organic samples without contact to an aqueous phase, several different fragments were built with increasing yield towards increasing dose (Fig. 4). Products with heavier and lighter masses were detected suggesting also the degradation of extractant molecules.

In samples irradiated in contact with nitric acid, mainly one product was found with $m/z = 663.4$ u, which may be an addition product of one 1-octanol molecule to the CyMe₄BTBP molecule. However, the HPLC-MS method does not give structural information. Lighter masses than the $M + H^+$ peak were only observed in negligible abundances.

The radiolysis of alcohols, such as isopropanol or hexanol, mainly results in the highly reactive α -hydroxy radicals as described in the literature by Eqs. (1)–(4) [25–29]. The reaction of diluent radicals with extractant molecules was reported as sensitization effect [30, 31].

- (1) $RCH_2OH + \rightarrow [RCH_2OH]^*$
- (2) $[RCH_2OH]^* \rightarrow e^- + [RCH_2OH]^{*+}$
- (3) $e^- \rightarrow e^-_{solv}$
- (4) $[RCH_2OH]^{*+} + RCH_2OH \rightarrow RC^{\bullet}HOH + RCH_2OH_2^+$

According to this mechanism, it is very likely that during irradiation experiments, α -hydroxyoctyl

Fig. 4. CyMe₄BTBP irradiated without contact to an aqueous phase to an absorbed dose of 100 kGy.

Table 1. Calculated mass to charge ratios for CyMe₄BTBP and α -hydroxyoctyl adducts. ($M = \text{CyMe}_4\text{BTBP}$; $X = \alpha$ -hydroxyoctyl ($\text{CH}_3(\text{CH}_2)_6\text{C}^{\bullet}\text{HOH}$))

	Calculated m/z ratio	Molecular formula
$M + H^+$	535.33 u	$\text{C}_{32}\text{H}_{39}\text{N}_8^+$
$M + X + H^+$	663.45 u	$\text{C}_{40}\text{H}_{55}\text{N}_8\text{O}^+$
$M + 2X + H^+$	791.57 u	$\text{C}_{48}\text{H}_{71}\text{N}_8\text{O}_2^+$

Fig. 5. CyMe₄BTBP irradiated in contact to 1 mol/L HNO_3 to an absorbed dose of 100 kGy.

radicals were formed and reacted with the ligand molecule. This is in good agreement with the observed m/z ratios, especially in samples irradiated in contact with nitric acid, where exclusively $M + X + H^+$ ($X = \alpha$ -hydroxyoctyl ($\text{CH}_3(\text{CH}_2)_6\text{C}^{\bullet}\text{HOH}$)) was found (Table 1, Fig. 5). Based on the results from the liquid-liquid extraction, we assume that the reaction of the α -hydroxyoctyl is taking place on the ‘periphery’ of the ligand molecule. The tetradentate binding pocket made up by the nitrogen donor groups of CyMe₄BTBP, should not be occupied [32]. In the literature, radiolysis of nitric acid is well described and especially radical scavenging by HNO_3 , NO_3^- or H^+ seems to be likely [33–40]. The individual influences of HNO_3 , NO_3^- or H^+ will therefore be investigated and further detailed investigations of the radiolysis mechanism are planned (e.g. using pulse radiolysis). In samples irradiated without contact with an aqueous phase, also the higher addition product containing two α -hydroxyoctyl groups ($M + 2X + H^+$) was found (Fig. 4). The m/z ratio of this species is 791.75 which is present in the sample at a relatively low abundance. The dominating species is found to be $M + 2X + \text{H}_2 + \text{H}^+$ ($m/z = 793.59$). This observation is also true for the $M + X$ product. This seems to be the product of the reduction of one of the double-bonds in the molecule.

Conclusions and outlook

The gamma radiolysis of the highly selective nitrogen donor ligand CyMe₄BTBP was investigated in solution and the influence of nitric acid contact during irradiation was tested. A protection of CyMe₄BTBP against radiolytic degradation was found for solutions irradiated in contact with nitric acid. In contrast to irradiation experiments without contact to nitric acid solutions, no decrease in ^{241}Am and ^{152}Eu distribu-

tion ratios was observed. As nitric acid is commonly used in partitioning processes for trivalent actinide separation, this protective effect plays a crucial role for the long-term performance of the used solvents.

A large number of radiolysis products was found in qualitative HPLC-MS measurements of samples irradiated without contact to an aqueous phase. In contrast, only the formation of 1-octanol adducts to the extractant was observed in samples irradiated in contact with nitric acid. The protective effect of nitric acid reduced the formation of other degradation products and the adducts are believed to potentially be able to extract trivalent actinides, as distribution ratios remained constant.

As the next step, it is planned to perform high resolution mass spectroscopy to further identify the radiolysis products and to synthesize 1-octanol adducts to CyMe₄BTBP. These synthesized molecules will then also be tested for their extraction abilities within the current European SACSESS project. Additionally, the CyMe₄BTBP molecule, which is the current reference molecule in European research, will be compared to the very promising molecule CyMe₄BTPPhen, where the bipyridine moiety is replaced by a phenanthroline functionality to fix the molecule in the *cis*-conformation resulting in a thermodynamically more favored metal-ligand complexation.

Acknowledgments. Financial support for this research is provided by the European Atomic Energy Community's 7th Framework Programme project SACSESS – grant agreement no. FP7-Fission-2012-323-282.

References

1. OECD-NEA. (2011). *Potential benefits and impacts of advanced nuclear fuel cycles with actinide partitioning and transmutation*. Issy-les-Moulineaux, France: O. Publishing OECD-NEA. (NEA no. 6894).
2. González-Romero, E. M. (2011). Impact of partitioning and transmutation on the high level waste management. *Nucl. Eng. Des.*, 241, 3436–3444. DOI: 10.1016/j.nucengdes.2011.03.030.
3. Modolo, G., Geist, A., & Miguiditchian, M. (2015). Minor actinide separations in the reprocessing of spent nuclear fuels: recent advances in Europe. In R. Taylor (Ed.), *Reprocessing and recycling of spent nuclear fuel* (pp. 245–287). Oxford: Woodhead Publishing.
4. 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.
5. 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.
6. Malmbeck, R., Courson, O., Pagliosa, G., Romer, K., Satmark, B., Glatz, J. P., & Baron, P. (2000). Partitioning of minor actinides from HLLW using the DIAMEX process. Part 2 – “Hot” continuous counter-current experiment. *Radiochim. Acta*, 88, 865–871. DOI: 10.1524/ract.2000.88.12.865.
7. Geist, A., Hill, C., Modolo, G., Foreman, M. R. S. J., Weigl, M., Gompper, K., Hudson, M. J., & Madic, C. (2006). 6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl)[2,2']bipyridine, an effective extracting agent for the separation of americium(III) and curium(III) from the lanthanides. *Solvent Extr. Ion Exch.*, 24, 463–485. DOI: 10.1080/07366290600761936.
8. Foreman, M. R. S., Hudson, M. J., Drew, M. G. B., Hill, C., & Madic, C. (2006). Complexes formed between the quadridentate, heterocyclic molecules 6,6'-bis-(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2'-bipyridine (BTBP) and lanthanides(III): implications for the partitioning of actinides(III) and lanthanides(III). *Dalton Trans.*, 13, 1645–1653. DOI: 10.1039/B511321k.
9. Magnusson, D., Christiansen, B., Foreman, M. R. S., Geist, A., Glatz, J. P., Malmbeck, R., Modolo, G., Serrano-Purroy, D., & Sorel, C. (2009). Demonstration of a SANEX process in centrifugal contactors using the CyMe₄-BTBP molecule on a genuine fuel solution. *Solvent Extr. Ion Exch.*, 27, 97–106. DOI: 10.1080/07366290802672204.
10. Wilden, A., Schreinemachers, C., Sypula, M., & Modolo, G. (2011). Direct selective extraction of actinides (III) from PUREX raffinate using a mixture of CyMe₄BTBP and TODGA as 1-cycle SANEX solvent. *Solvent Extr. Ion Exch.*, 29, 190–212. DOI: 10.1080/07366299.2011.539122.
11. Magnusson, D., Geist, A., Wilden, A., & Modolo, G. (2013). Direct selective extraction of actinides (III) from PUREX raffinate using a mixture of CyMe₄-BTBP and TODGA as 1-cycle SANEX solvent. Part II: Flow-sheet design for a counter-current centrifugal contactor demonstration process. *Solvent Extr. Ion Exch.*, 31, 1–11. DOI: 10.1080/07366299.2012.700596.
12. Wilden, A., Modolo, G., Schreinemachers, C., Sadowski, F., Lange, S., Sypula, M., Magnusson, D., Geist, A., Lewis, F. W., Harwood, L. M., & Hudson, M. J. (2013). Direct selective extraction of actinides (III) from PUREX raffinate using a mixture of CyMe₄BTBP and TODGA as 1-cycle SANEX solvent. Part III: Demonstration of a laboratory-scale counter-current centrifugal contactor process. *Solvent Extr. Ion Exch.*, 31, 519–537. DOI: 10.1080/07366299.2013.775890.
13. Mincher, B. J. (2010). An overview of selected radiation chemical reactions affecting fuel cycle solvent extraction. *ACS Symp. Ser.*, 1046, 181–192. DOI: 10.1021/bk-2010-1046.ch015.
14. Hill, C., Berthon, L., & Madic, C. (2005). Study of the stability of BTP extractants under radiolysis. In Proceedings of the GLOBAL 2005, 9–13 October (p. 283). Tsukuba, Japan.
15. Retegan, T., Ekberg, C., Englund, S., Fermvik, A., Foreman, M. R. S., & Skarnemark, G. (2007). The behaviour of organic solvents containing C5-BTBP and CyMe₄-BTBP at low irradiation doses. *Radiochim. Acta*, 95, 637–642. DOI: 10.1524/ract.2007.95.11.637.
16. Fermvik, A., Berthon, L., Ekberg, C., Englund, S., Retegan, T., & Zorz, N. (2009). Radiolysis of solvents containing C5-BTBP: identification of degradation products and their dependence on absorbed dose and dose rate. *Dalton Trans.*, 32, 6421–6430. DOI: 10.1039/b907084b.
17. Fermvik, A., Ekberg, C., Englund, S., Foreman, M. R. S. J., Modolo, G., Retegan, T., & Skarnemark, G. (2009). Influence of dose rate on the radiolytic stability of a BTBP solvent for actinide(III)/lanthanide(III)

- separation. *Radiochim. Acta*, 97, 319–324. DOI: 10.1524/ract.2009.1615.
18. Magnusson, D., Christiansen, B., Malmbeck, R., & Glatz, J. P. (2009). Investigation of the radiolytic stability of a CyMe₄-BTBP based SANEX solvent. *Radiochim. Acta*, 97, 497–502. DOI: 10.1524/ract.2009.1647.
 19. Fermvik, A., Aneheim, E., Grüner, B., Hájková, Z., Kvicalová, M., & Ekberg, C. (2012). Radiolysis of C5-BTBP in cyclohexanone irradiated in the absence and presence of an aqueous phase. *Radiochim. Acta*, 100, 273–282. DOI: 10.1524/ract.2012.1908.
 20. Mincher, B. J., Modolo, G., & Mezyk, S. P. (2010). Review: The effects of radiation chemistry on solvent extraction 4: Separation of the trivalent actinides and considerations for radiation-resistant solvent systems. *Solvent Extr. Ion Exch.*, 28, 415–436. DOI: 10.1080/07366299.2010.485548.
 21. Sulich, A., Grodkowski, J., Mirkowski, J., & Kocia, R. (2014). Reactions of ligands from BT(B)P family with solvated electrons and benzophenone ketyl radicals in 1-octanol solutions. Pulse radiolysis study. *J. Radioanal. Nucl. Chem.*, 300, 415–421. DOI: 10.1007/s10967-014-3021-5.
 22. Mincher, B. J., & Mezyk, S. P. (2009). Radiation chemical effects on radiochemistry: A review of examples important to nuclear power. *Radiochim. Acta*, 97, 519–534. DOI: 10.1524/ract.2009.1646.
 23. Mincher, B. J., Modolo, G., & Mezyk, S. P. (2009). The effects of radiation chemistry on solvent extraction: 1. Conditions in acidic solution and a review of TBP radiolysis. *Solvent Extr. Ion Exch.*, 27, 1–25. DOI: 10.1080/07366290802544767.
 24. Mincher, B. J. (2015). Radiation chemistry in the reprocessing and recycling of spent nuclear fuels. In R. Taylor (Ed.), *Reprocessing and recycling of spent nuclear fuel* (pp. 191–211). Oxford: Woodhead Publishing.
 25. Nilsson, M., Andersson, S., Ekberg, C., Foreman, M. R. S., Hudson, M. J., & Skarnemark, G. (2006). Inhibiting radiolysis of BTP molecules by addition of nitrobenzene. *Radiochim. Acta*, 94, 103–106. DOI: 10.1524/ract.2006.94.2.103.
 26. Mincher, B. J., Arbon, R. E., Knighton, W. B., & Meikrantz, D. H. (1994). Gamma-ray-induced degradation of PCBs in neutral isopropanol using spent reactor-fuel. *Appl. Radiat. Isot.*, 45, 879–887. DOI: 10.1016/0969-8043(94)90219-4.
 27. Freeman, G. R. (1970). Radiolysis of alcohols. *Actions Chim. Biol. Radiat.*, 14, 73–134.
 28. Mincher, B. J., Mezyk, S. P., Elias, G., Groenewold, G. S., Riddle, C. L., & Olson, L. G. (2013). The radiation chemistry of CMPO: Part 1. Gamma radiolysis. *Solvent Extr. Ion Exch.*, 31, 715–730. DOI: 10.1080/07366299.2013.815491.
 29. Symons, M. C. R., & Eastland, G. W. (1977). Radiation mechanisms. Part 18. The radiolysis of alcohols: an electron spin resonance study. *J. Chem. Res., Suppl.*, 254–255.
 30. Sugo, Y., Sasaki, Y., & Tachimori, S. (2002). Studies on hydrolysis and radiolysis of N,N,N',N'-tetraoctyl-3-oxapentane-1,5-diamide. *Radiochim. Acta*, 90, 161–165. DOI: 10.1524/ract.2002.90.3_2002.161.
 31. Sugo, Y., Izumi, Y., Yoshida, Y., Nishijima, S., Sasaki, Y., Kimura, T., Sekine, T., & Kudo, H. (2007). Influence of diluent on radiolysis of amides in organic solution. *Radiat. Phys. Chem.*, 76, 794–800. DOI: 10.1016/j.radphyschem.2006.05.008.
 32. Steppert, M., Cisarova, I., Fanghanel, T., Geist, A., Lindqvist-Reis, P., Panak, P., Stepnicka, P., Trumm, S., & Walther, C. (2012). Complexation of europium(III) by bis(dialkyltriazinyl)bipyridines in 1-octanol. *Inorg. Chem.*, 51, 591–600. DOI: 10.1021/ic202119x.
 33. Mezyk, S. P., Cullen, T. D., Elias, G., & Mincher, B. J. (2010). Aqueous nitric acid radiation effects on solvent extraction process chemistry. *ACS Symp. Ser.*, 1046, 193–203. DOI: 10.1021/bk-2010-1046.ch016.
 34. Mincher, B. J. (2012). Degradation issues in aqueous reprocessing systems. *Compr. Nucl. Mater.*, 5, 367–388. DOI: 10.1016/b978-0-08-056033-5.00104-x.
 35. Mincher, B. J., Mezyk, S. P., & Martin, L. R. (2008). A pulse radiolysis investigation of the reactions of tributyl phosphate with the radical products of aqueous nitric acid irradiation. *J. Phys. Chem. A*, 112, 6275–6280. DOI: 10.1021/jp802169v.
 36. Harwood, L. M., Lewis, F. W., Hudson, M. J., John, J., & Distler, P. (2011). The separation of americium(III) from europium(III) by two new 6,6'-bistriazinyl-2,2'-bipyridines in different diluents. *Solvent Extr. Ion Exch.*, 29, 551–576. DOI: 10.1080/10496475.2011.556989.
 37. Joshi, R., Pathak, P. N., Manchanda, V. K., Sarkar, S. K., & Mukherjee, T. (2010). Reactions of N,N-dihexyloctanamide with nitrate and dodecane radicals: a pulse radiolysis study. *Res. Chem. Intermed.*, 36, 503–510. DOI: 10.1007/s11164-010-0161-2.
 38. Neta, P., & Huie, R. E. (1986). Rate constants for reactions of nitrogen oxide (NO₃) radicals in aqueous solutions. *J. Phys. Chem.*, 90, 4644–4648. DOI: 10.1021/j100410a035.
 39. Katsumura, Y. (1998). NO₂[•] and NO₃[•] radicals in radiolysis of nitric acid solutions. In Z. B. Alfassi (Ed.), *The chemistry of free radicals: N-centered radicals* (pp. 393–412). Weinheim: Wiley.
 40. Katsumura, Y., Jiang, P. Y., Nagaishi, R., Oishi, T., Ishigure, K., & Yoshida, Y. (1991). Pulse radiolysis study of aqueous nitric acid solutions: formation mechanism, yield, and reactivity of NO₃ radical. *J. Phys. Chem.*, 95, 4435–4439. DOI: 10.1021/j100164a050.