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Solvent extraction systems for mutual separation of Am(III) and Cm(III) from nitric acid solutions. A review of recent state-of-the-art

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ABSTRACT

Americium and curium, present in spent nuclear fuel, are carried forward to the high-level wastes (HLW) upon its reprocessing within the closed nuclear fuel cycle strategy. These minor actinides are required to be extracted efficiently to mitigate the long-term radiotoxicity of the HLW, which in some countries is the proposed strategy for the safe management of radioactive wastes emanating from the reprocessing of spent nuclear fuel. While both Am and Cm are co-extracted by most of extractants used for actinide partitioning and lanthanide-actinide separations, their mutual separation makes Am transmutation less complicated. In their most stable (trivalent) oxidation state, these elements are very difficult to separate. In this review, solvent extraction systems for the mutual separation of Am(III) and Cm(III) from nitric acid solutions are discussed. The extraction systems for the separation of americium directly from high-level liquid waste and from isolated mixtures of americium and curium are considered.

Abbreviations: D : distribution ratio, $D = \frac{C_{org}}{C_{aq}}$, where C_{org} – total concentration of a metal in the organic phase, C_{aq} – total concentration of a metal in the aqueous phase; DF : decontamination factor, $DF = \frac{C_{x,feed} \cdot Q_{feed}}{C_{x,product} \cdot Q_{product}}$, where $C_{x,feed}$, $C_{x,product}$ – concentrations of an impurity in the initial feed solution and the product solution (raffinate or back-extract), Q_{feed} , $Q_{product}$ – flow rates of the initial feed solution and the product solution; $GW \times day/tHM$: burn-up of nuclear fuel, where tHM – tons of heavy metal; HAC: high active concentrate; HLW: high level waste; HSAB: Hard and Soft Lewis Acids and Bases; K_{ex} : constant of extraction, for the reaction $M^{3+}_{(aq)} + 3NO_3^{-}_{(aq)} + nL_{(org)} = M(NO_3)_3L_n_{(org)}$, $K_{ex} = \frac{[M^{3+}][NO_3^{-}]^3[L]^n}{[M(NO_3)_3L_n]}$; PUREX: Plutonium Uranium Reduction EXtraction; GANEX: Grouped ActiNide EXtraction; REE: rare earth element; SF: separation factor, $SF = D_1/D_2$, $D_1 > D_2$; SNF: spent nuclear fuel; TRLIFS: time-resolved laser induced fluorescence spectrometry; β : constant of complex formation;

KEYWORDS

Solvent extraction; americium; curium; separation; high-level wastes; radioactive waste

List of ligands: ADAAM(EH): tetra-(2-ethylhexyldiamide-(2-ethylhexyl)-amine; BTPPhen: bis-triazinylphenanthroline; (Cl-Ph)₂PS 2H: bis-(chlorophenyl)-dithiophosphinic acid; CMPO: Carbamoyl methylphosphine oxide DMDOHEMA: *N,N'*-dimethyl-*N,N'*-diocetyl-2-(hexyloxy)ethylmalonamide; DOODA: *N,N,N',N'*-tetraalkyl-3,6-dioxaoctanediamide; H2BP18C6: *N,N'*-bis[(6-carboxy-2-pyridyl)methyl]-1,10-diaza-18-crown-6; H4TPAEN: *N,N,N',N'*-tetrakis-[(6-carboxypyridin-2-yl)-ethylenediamine; HDEHP: di-(2-ethylhexyl)phosphoric acid; HEDTA: hydroxyethylethylenediaminetriacetic acid; HEH[EHP]: 2-ethylhexylphosphonic acid; NTAamide: *N,N,N,N',N',N'*-hexaalkylnitrilotriacetamide; PhPyPO: phenyl-pyridine phosphine oxide; TBP: tri-(*n*-butyl)phosphate; TEDGA: tetraethyldiglycolamide; TEHP: tri-(2-ethylhexyl) phosphate; TODGA: tetraoctyldiglycolamide; TPH: hydrogenated tetrapropylene

List of terms: CHON-principle: An idea that the extractant molecule should consist only of carbon, hydrogen, oxygen and nitrogen atoms, so that the spent ligand can be easily incinerated without the formation of any solid waste. Salting out-agent: An inorganic salt with the same counter-ion as an extracted complex has. Counter-current process: A process in which the solvent and the aqueous feed streams, in contact with each other, flow in opposite directions.

Introduction

Nuclear power remains the most important source of energy that has the lowest carbon dioxide emissions.^[1] However, the main problems of its sustainable development include the accumulation of spent nuclear fuel (SNF) in an open fuel cycle (or once-through cycle) and the safe management of the radioactive wastes generated during the SNF reprocessing in a closed fuel cycle.

The main goal of the reprocessing of UO₂ or (U,Pu)O₂ based SNFs is the extraction of valuable components – uranium and plutonium that can be re-used in the nuclear fuel cycle once again in thermal or fast neutron reactors. PUREX process (Plutonium Uranium Reduction EXtraction) is used today in several countries on an industrial scale for SNF reprocessing. PUREX is a process based on the dissolution of spent nuclear fuel in nitric acid with subsequent liquid-liquid extraction of uranium(VI) and plutonium(IV) by tri-*n*-butyl phosphate (TBP) in a paraffinic hydrocarbon-based diluent. The resulting raffinate (aqueous phase after extraction) of the first stage of the PUREX process is termed as high active waste or HAW which is concentrated and denitrated^[2] to result in the so-called High Level Waste (HLW). The reprocessing of 1 t of uranium oxide spent fuel used in a thermal neutron reactor with a burn-up of 33 GW×day/tHM and a cooling period of 3 years generates approximately 5 m³ of raffinate with total β + γ activity of c.a. 10¹⁷ Bq.^[3]

The composition of HLW can be divided into three groups. First are the products of nuclear fission of uranium-235 and plutonium-239, which include elements ranging from arsenic to lanthanides^[4]; the yield of fission products

has a double-humped dependence on the atomic mass with maxima at 90 and 140 a.m.u.^[5]

Second are the products of neutron activation and corrosion products of equipment and fuel cladding. Third are the actinides – mainly the unextracted uranium and plutonium remaining after the PUREX process, and minor actinides viz. neptunium, americium, and curium.

In general, there are two ways of safe managing the HLW. The first is the immobilization, wherein all HLW components are calcined and incorporated in a stable matrix (which is now glass) with subsequent long-term storage in an underground repository. The disadvantage of this approach is the complexity of the selection of a universal matrix, which must include and safely retain the entire spectrum of radionuclides for the time period of up to 10^6 years,^[6,7] and large surveillance costs.

Another approach is the partitioning and transmutation strategy, wherein, the long-lived components (with $t_{1/2} > 1000$ years) of the HLW viz. the minor actinides and certain fission product elements are preferentially separated according to their chemical and nuclear-physical properties.^[4,8] For example, only elements with similar chemical properties can be extracted (e.g., tri-valent *f*-elements, or highly soluble elements like mono- and di-valent *s*-elements, Cs, Sr, etc.), or radionuclides can be separated due to their ability to capture neutrons. Selection of the matrix for immobilization of a specific radionuclide or a group of elements with similar chemical properties is much easier. Isolation of strontium-90 and cesium-137 will reduce waste heat generation and MANREM^[9] issues (particularly for the latter), and the radionuclides themselves can be used as radioactive sources for many applications. Also, there is a possibility to use the nuclear spallation reaction for transmutation of some of these radionuclides viz. the minor actinides.^[10] Another advantage of the concept of partitioning is the extraction of platinum group elements (Pd, Ru, Rh), which can be used in different applications, for example, in catalysts or as a very durable cover for a matrix of HLW.^[11]

Another important point is transmutation of americium-241,243, and neptunium-237 in the 4th generation reactors.^[12–14] These processes will result in the formation of radionuclides with significantly shorter half-lives (maximum to tens of years), which will lead to a significant reduction of long-term activity of radioactive waste^[15] as well as waste heat generation that allows increasing the total capacity of the deep geological repository.^[16] Thus, the partitioning and transmutation concept can benefit from a more compact repository for the same amount of long-lived HLW.

It is obvious that this approach requires the solution of complex chemical problems associated with the isolation of the individual elements from HLW. Neptunium recovery from HLW can be relatively easily performed by changing its oxidation state as Np(IV) and Np(VI) are efficiently extracted by TBP.^[17–19]

The americium isolation stage can be performed during sequential extraction processes (for example, a series of PUREX-DIAMEX-LUCA processes^[20])

Table 1. The main neutron poisons from fission products. Neutron capture cross sections and total yield for radionuclides are taken from,^[22] stable lanthanides' (Ln) yields are taken from,^[23] cross sections for Gd isotopes are taken from^[24].

Nuclide	Cross section, barn	Yield, %	$t_{1/2}$
Xe-135	2.65×10^6	6.61	9.2 h
Sm-149	4.01×10^4	1.10	stable
Sm-151	1.53×10^4	0.42	88.8 y
Gd-157	2.54×10^5	0.015	stable
Gd-155	6.07×10^4	0.05	stable
Pm-147	1.68×10^2	2.23	2.62 y
Eu-151	9.2×10^3	-	5×10^{18} y

Table 2. Half-life values for different actinides and probability of spontaneous fission,^[26] neutron yield in neutron/g \times s for spontaneous fission and (α ,n)-reaction in AnO_2 in terms of g of metal are taken from^[26].

Radionuclide	$t_{1/2}$, years	Probability of spontaneous fission, %	Neutrons yield, n/(sec \times g(An))	
			Fission	(α ,n)
U-235	$7.1 \cdot 10^8$	$7 \cdot 10^{-9}$	-	-
Np-237	$2.1 \cdot 10^6$	$2.1 \cdot 10^{-10}$	$1.14 \cdot 10^{-4}$	0.34
Pu-239	$2.4 \cdot 10^4$	$3.1 \cdot 10^{-10}$	$2.18 \cdot 10^{-2}$	38.1
Am-241	$4.3 \cdot 10^2$	$3.6 \cdot 10^{-10}$	1.18	$2.69 \cdot 10^3$
Am-243	$7.3 \cdot 10^3$	$3.7 \cdot 10^{-9}$	3.93	$1.34 \cdot 10^2$
Cm-244	18.1	$1.4 \cdot 10^{-4}$	$1.08 \cdot 10^7$	$7.73 \cdot 10^4$
Cm-242	0.3	$6.2 \cdot 10^{-6}$	$2.1 \cdot 10^7$	$3.76 \cdot 10^6$
Cf-252	2.6	3.092	$2.34 \cdot 10^{12}$	$6 \cdot 10^5$

or directly from PUREX-raffinate (for example, the EXAm process^[21]), which requires selectivity to americium against the background of all elements presented in the HLW. While actinide partitioning extractants viz. CMPO (carbamoylmethylphosphine oxide), malonamides, diglycolamides, etc. can extract the trivalent actinides, the trivalent lanthanides present in the HLW are co-extracted. The most difficult task is the separation of trivalent actinides from the lanthanides and even more challenging is the separation of Am and Cm. This separation is necessary for the following reasons:

- (1) Lanthanides are neutron poisons – some isotopes have high neutron capture cross sections (see Table 1). Their presence in the fuel (or irradiated target) together with the minor actinides will inhibit the transmutation of americium^[20,25]
- (2) The involvement of curium-242,244 in the closed fuel cycle is problematic because it has a high neutron and heat emission (Table 2). For this reason, the presence of curium will complicate the fabrication and operation of nuclear fuel (or targets for irradiation). In addition, curium-244 can be used as the starting material for the production of californium-252,^[27–29] a radionuclide that is used as a neutron source in many applications including in nuclear medicine. Thus, curium must be isolated in the individual form.

The complexity of the Ln, Am and Cm separation is determined by the similarity in their chemical properties, i.e.^[30,31]:

1. Most of transplutonium elements and lanthanides are late 5 *f*- and 4 *f*-elements, respectively, which are characterized by the filling of the inner *f*-orbitals with increasing atomic number. This has a little effect on the chemical properties, which are mainly dependent on processes in the outer electron shells. In view of this, these elements predominantly exist in the +3 oxidation state in aqueous solutions.
2. The ionic radii of these cations are comparable. Americium and curium ions have isostructural analogues in the series of lanthanides: $r(\text{Nd}^{3+}) \approx r(\text{Am}^{3+})$, $r(\text{Sm}^{3+}) \approx r(\text{Cm}^{3+})$. This makes it almost impossible to separate the trivalent minor actinides (Am and Cm) from lanthanides by adjusting only the size of the coordination sphere of the organic ligands.

The main differences between these cations are:

1. The higher tendency of actinides to form covalent bonds in comparison with the lanthanides. The 5 *f*-orbitals of actinides are closer in energy to the outer orbitals than the 4 *f*-orbitals of lanthanides. Thus, the *f*-orbitals of these actinides can be involved in the formation of covalent bonds.^[32,33] In terms of the Pearson's HSAB theory,^[34–36] Am^{3+} and Cm^{3+} are softer acids in comparison with the lanthanide cations. On the other hand, this difference is insignificant for the americium-curium pair.
2. Americium can be oxidized up to the oxidation state of +6. This changes its extraction behavior dramatically.^[37,38,39] But it also makes separation process more complicated due to the very low stability of the higher oxidation states (AmO_2^{2+} or AmO_2^+) which are easily reduced by the construction materials (e.g. steel), the organic solvents and due to radiolysis.^[40]

At the moment, there are a number of reviews related to the fractionation of high-level waste^[20,41–46] or to particular classes of extractants.^[41,47–49] These papers are mainly focused on the group separation of Am(III) and Cm(III) from high-level wastes and on the complexity of their separation from lanthanides(III). Fewer work is carried out related to the separation of valuable components of the HLW – for example, palladium.^[50]

In view of the chemical similarity of Am and Cm, their extraction is comparable and hence, the separation factor values of Am(III)-Cm(III) pair for the main classes of extractants (esters of phosphoric acid, CMPO, malonamides, diglycolamides) are usually less than 2 (Table 3).

In hydrometallurgical processing of stable elements, such values of separation factor allow separation using hundreds of stages in a counter-current process (e.g., the isolation of individual rare-earth elements using tri-*n*-butyl-

Table 3. Am-Cm separation factor for some classes of extractants.

Extractant	Conditions	SF _{Cm/Am}	Reference
TBP	30% TBP in kerosene, 0–6 M HNO ₃ /LiNO ₃ /Al(NO ₃) ₃	<1.4	[51]
TOPO	5% TOPO in xylene 0.01–0.5 M HNO ₃ /NH ₄ NO ₃	1.2–1.5	[52]
CMPO	CMPO as extraction chromatography sorbent, 0.01–10 M HNO ₃	<1.45	[53]
DMDOHEMA	0.65 M DMDOHEMA in TPH (hydrogenated tetrapropylene), 0.5–2.5 M HNO ₃	1.5	[54]
TODGA	0.2 TODGA in TPH with 5% 1-octanol, 1 M HNO ₃	1.2	[55]

phosphate^[56–58]). However, high specific activity of the HLW significantly complicates using such a huge number of stages in the counter-current process due to the radiolysis of the extraction system components (mainly organic compounds). Negative effect of radiolysis can be reduced by increasing the separation factor. Thus, it is better for the liquid-liquid extraction systems to have the separation factor ($SF = D_{Am}/D_{Cm}$) values greater than 2 to allow efficient separation of Am(III), Cm(III) and Ln(III) in industrial scale.

The aim of this review is to describe a limited number of such systems developed in the last 20 years and to discuss the chemistry behind the improved separation behavior. As nitric acid solutions are involved in the SNF reprocessing as well as other radioactive waste processing schemes including actinide partitioning and lanthanide actinide separations, here we describe only the extraction studies from nitric acid solutions.

2. Extraction systems for americium(III) and curium(III) separation without the addition of water-soluble ligands

2.1. Synergistic mixture of bis-(chlorophenyl)dithiophosphinic acid and tri-(2-ethylhexyl) phosphate

The first extraction system with a high selectivity for americium vis-à-vis curium was a synergistic mixture of 0.5 M bis-(chlorophenyl)dithiophosphinic acid (Figure 1a) and 0.25 M tri-(2-ethylhexyl) phosphate (Figure 1b). The separation factors of americium-europium and americium-curium pairs are reported to be as high as 2000 and 8, respectively.^[54] Also, all lanthanides have lower distribution ratios than curium, so Am(III) can be separated from both

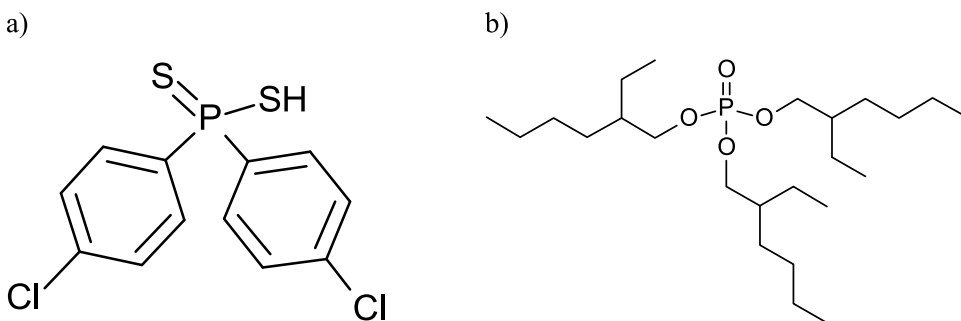


Figure 1. Structural formulae of a) bis-(chlorophenyl)-dithiophosphinic acid ((Cl-Ph)₂PS₂H); b) tri-(2-ethylhexyl) phosphate (TEHP).

Cm(III) and Ln(III) ions. Extraction was studied using aqueous solutions of 0.1 M nitric acid and 0.9 M sodium nitrate. Higher nitric acid concentration suppressed the extraction of the metal ions: at $C(\text{HNO}_3) > 1 \text{ M}$, $D_{\text{Am}} < 0.001$, the separation factor for the americium-curium pair remained as high as 8–10.^[59]

The experimentally determined thermodynamic parameters revealed that the entropy factor was responsible for the observed selectivity.^[60] The stoichiometry of the extracted complexes was investigated by the slope analysis method that showed the formation of mixed complexed species such as $\text{Me}((\text{Cl-Ph})_2\text{PS}_2)_3(\text{TEHP})_x$, where $x = 1$ for Am and Cm, $x = 2$ or 3 for lanthanides. Also, it was found that the metal ion extraction doesn't occur in the absence of a neutral extractant ($D_{\text{Am}}, D_{\text{Eu}} < 10^{-3}$).^[61]

This extraction system was also tested in dynamic mode (see section 3.2.3.3).

Tetra-(2-ethylhexyldiamide-(2-ethylhexyl)-amine (ADAAM(EH))

ADAAM is a series of alkyl diamide amines (Figure 2) containing N,O-donor atoms as binding centers. For 0.2 M organic solutions of ADAAM(EH) ligand (tetra-(2-ethylhexyldiamide-(2-ethylhexyl)-amine; in Figure 2, $R_1 = R_2 = 2\text{-ethylhexyl}$), $\text{SF}_{\text{Am/Cm}}$ is equal to 5.5 in a wide range of acid concentration (1–5 M HNO_3).^[62] This ligand was relatively simple to synthesize, satisfied the CHON^[63] principle (see List of terms) and was found to be highly soluble in non-polar solvents such as kerosene.^[64] ADAAM derivatives with *n*-octyl substituents at nitrogen atoms or their combination with 2-ethylhexyl ones were also investigated. The extraction efficiency of these ligands was significantly lower than that of ADAAM(EH), and the data on $\text{SF}_{\text{Am/Cm}}$ were not reported.^[65] It should also be noted that the first ligand of a similar nature was described in the same work as the predecessor of TODGA (*N,N,N',N'*-tetra-*n*-octyl-diglycol amide).^[66]

In the theoretical study^[67] of americium and curium complexes with ADAAM ligand ($R_1 = R_2 = \text{Me}$) and DGA analogue it was shown that the main difference is the degree of metal 5 *f*-electrons participation in the covalent bonding in the complexes.

This extraction system was also tested in dynamic mode (see section 3.2.3.4).

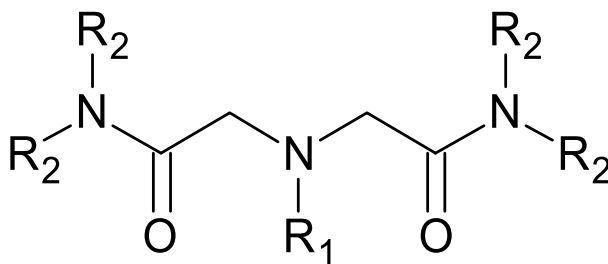


Figure 2. General structure of the ADAAM ligands. ADAAM(EH)– $R_1 = R_2 = 2\text{-ethylhexyl}$.

Ligands containing *N*-heterocycles

N,O-donor heterocyclic ligands

A high selectivity of EtpHexPhClPhen ligand^[68] (Figure 3a) towards americium in the presence of curium has been established from 0.5 to 5 M nitric acid. The achieved $SF_{Am/Cm}$ values were as high as 4–5. It should be noted that a homolog of this ligand EtpEtPhPhen demonstrated significantly lower $SF_{Am/Cm}$ values – ca. 2. The authors pointed out that in the case of diamide of 2,6-pyridine- or 2,2'-bipyridyl-6,6'-dirboxylic acid, the length of the alkyl substituent does not affect the extraction properties significantly.^[69,70] Thus, the introduction of chlorine atoms in the 4- and 7-positions of the phenanthroline moiety is considered to be the reason of the increased selectivity.

Besides meta-nitro-benzotrifluoride, aliphatic alcohols and their mixtures with hydrocarbons can be used as diluents for this *N*-heterocyclic dicarboxamide. Main disadvantage of this ligand is its low stability in the presence of nitric acid and under gamma irradiation^[71] – in both cases, chlorine atoms are substituted by hydroxy-groups after more than one week of a phase contact time or after irradiation with an absorbed dose of 25 kGy.

Another example of *N*-heterocyclic ligand is the PhPyPO ligand (Figure 3b). The extraction system (0.001 M of PhPyPO in nitrobenzene) demonstrates $SF_{Am/Cm}$ values up to 3.5^[72] in a range of nitric acid concentrations of 0.1–3 M. Theoretical modeling of the americium and curium complexes structures attributed the observed selectivity to the small differences in the Me-N and Me-O bond distances.

Kinetic effects of *Am/Cm* separation in the case of CyMe₄-BTPhen

Bis-triazine heterocycles are well-known as highly selective ($SF_{Am/Eu} \approx 100$) extractants for the lanthanide(III) – actinide(III) group separation.^[49,73,74] Analogous phenanthroline-based ligands, where the structure of a triazinylphenanthroline (CyMe₄-BTPhen) was modified by introducing bromine or 4-hydroxyphenyl into the phenanthroline group (Figure 4), were also tested for the separation of americium and curium.^[75] This modification of the ligand led to an increase in the selectivity towards americium with respect to the lanthanides, and most

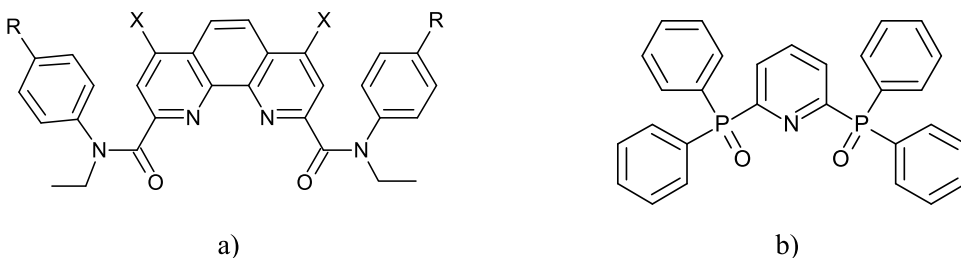


Figure 3. Structural formulae of (a): R = C_6H_{13} - and X = Cl – EtpHexPhClPhen, R = C_2H_5 - and X = H – EtpEtPhPhen and (b) PhPyPO ligands.

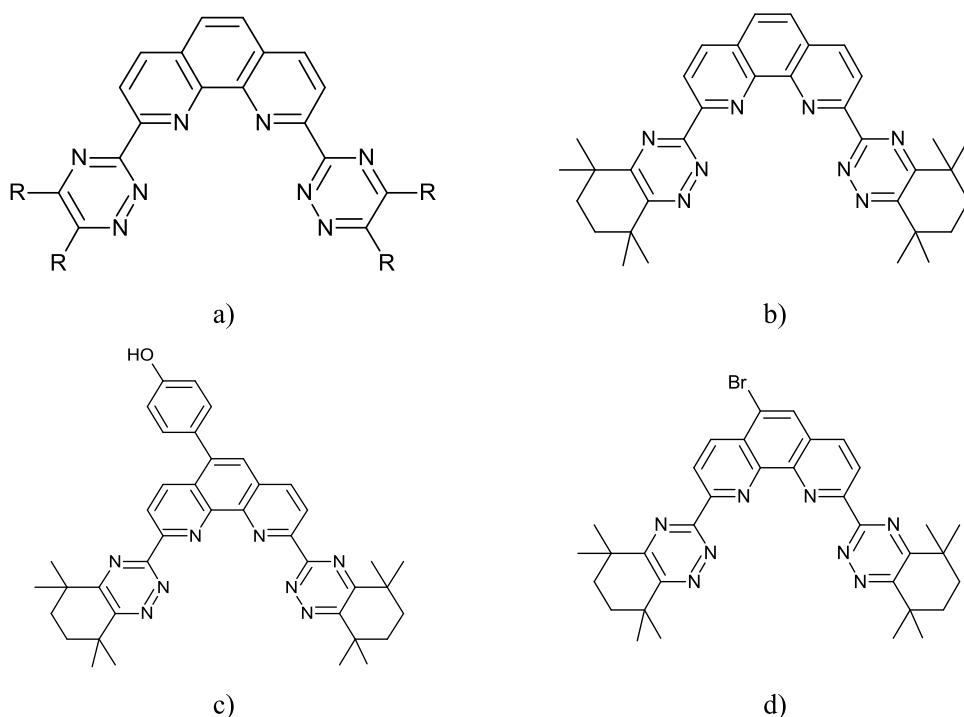


Figure 4. Structures of triazinylphenanthrolines: a) R-BTPhen, where R = C₄H₉, C₅H₁₁; b) CyMe₄-BTPhen; c) 5-(4-HOPh)CyMe₄-BTPhen; d) 5-Br-CyMe₄-BTPhen.

importantly – the separation of americium and curium. Thus, while a separation factor $SF_{Am/Eu} = 70$ was reported for CyMe₄-BTPhen from 3 M HNO₃, no selectivity have been established for americium and curium pair at any concentration of the acid. In the case of extraction with 5-Br-CyMe₄-BTPhen and 5-(4-HOPh)CyMe₄-BTPhen from 3 M HNO₃, the $SF_{Am/Eu}$ values were 680 and 320, respectively. The maximum value of $SF_{Am/Cm} = 7$ for 5-Br-CyMe₄-BTPhen was achieved in the case of extraction from 0.1 M HNO₃. For 5-(4-HOPh)CyMe₄-BTPhen, the maximum $SF_{Am/Cm} = 5$ was observed at 1 M HNO₃. However, no experimental details on the phase contact time was reported, and as mentioned below, may have significant effect on the separation behavior. It is worth highlighting that the extraction kinetics for the metal ions can be quite different and hence, the separation factors can change with contact time.

Interesting observations were made in a study where 5-bromo- or 5-(4-hydroxyl-phenyl) substituted CyMe₄-BTPhen was used and the $SF_{Am/Cm}$ values were obtained as a function of equilibration time.^[76] The $SF_{Am/Cm}$ value of ≈ 7 was achieved in a non-equilibrium state, which significantly decreased to ≈ 2 after attaining the extraction equilibrium which took about 2 h. While the metal ion extraction increased with an increase in the aqueous feed nitric acid concentration, the corresponding values of SF showed a decreasing trend. On the other hand, unsubstituted CyMe₄-BTPhen was also studied (0.01 M in 1-octanol), but

the $SF_{Am/Cm}$ values remained below 2 in the whole range of experimental conditions employed.

While a $SF_{Am/Cm}$ value of up to 4 was reported with $CyMe_4$ -BTPhen under controlled conditions^[77] (organic phase – 0.01 M $CyMe_4$ -BTPhen in a mixture of 1-octanol and toluene (40:60); aqueous phase – 4.0 M HNO_3), a significantly higher selectivity ($SF_{Am/Cm} = 7.9$) was reported when the feed was 2.4 M HNO_3 using an equilibration time of 10 h at a phase mixing rate of 250 rpm using half the ligand concentration.^[78] Under these conditions, equilibrium was not reached even after 22 hours, and the $SF_{Am/Cm}$ was found to decrease significantly to 1.7 though there was a sharp rise in the extraction of both the metal ions. On the contrary, increasing the mixing rate to 1800 rpm (ligand concentration was reduced to 0.001 M) resulted in the separation factor value of 4 after 20 minutes of phase contact. A similar “kinetic effect” was observed in cyclohexanone, but with shorter phase contact times (7–10 minutes) and with maximum $SF_{Am/Cm}$ values of 5–6 at 0.5 M HNO_3 and was seen to show a sharp decline at higher acid concentrations. Also, for the feed containing 0.5 M HNO_3 , the $SF_{Am/Cm}$ values sharply fell after 10 minutes to values close to 1 after reaching the equilibrium. The less pronounced “kinetic effect” of the separation of americium and curium was also shown for triazinyl-phenanthrolines with *n*-butyl and *n*-pentyl substituents in the triazinyl moieties with the maximum $SF_{Am/Cm}$ values of 3.1 and 2.6, respectively. The authors suggested that the main reason for the observed “kinetic effect” was the different kinetic labilities of the aqueous complexes of americium in comparison with those of curium. In their opinion, the dependence of the maximum separation factor on the type of substituents is associated with different hydrophobicity of the complexes formed by different ligands. Modeling of Am and Cm extraction process^[79] showed that the best model that fits experimental data is a mass-transfer as a rate-controlling process and calculated values of the overall mass-transfer coefficients confirmed that separation effect was caused by the different rates of Am(III) and Cm(III) extraction.

Extraction systems for Am/Cm separation in the presence of water-soluble ligands

One of the possible ways to increase the SF values without changing the medium and/or Am oxidations state is the addition of a water-soluble ligand with reverse selectivity, i.e., a water-soluble ligand should strongly bind to the metal ion, extracted to a lower extent in the organic phase component. In this case, it is possible to increase the separation factor to a value:

$$SF = SF_0 \frac{K_1}{K_2} \quad (1)$$

where SF_0 – separation factor in the absence of a water-soluble ligand, K_1 – the constant of complex formation for the lower extractable component with the

water-soluble ligand, K_2 – the constant of complex formation for the higher extractable component with the water-soluble ligand. In other words, the water-soluble ligand acts as a masking agent for the lower extractable component. This approach was used in the TALSPEAK process and all its subsequent modifications for An/Ln separation.^[80]

Further, extraction systems will be listed according to a more extractable component.

Extraction systems with preferential extraction of Am(III)

Extraction systems of this type are represented by various ligands in the organic phase, and diglycolamides with small alkyl chains are typically used as the water-soluble ligands.

In their studies,^[81,82] Sasaki et al. proposed two extraction systems using *N,N,N',N'*-tetraethyldiglycolamide (TEDGA) (Figure 5) as a masking agent for curium.

The first system was *N,N,N',N',N'',N''*-hexaalkyl nitrilotriacetamide (NTAamide) (Figure 6a) in *n*-dodecane as the extractant and TEDGA as the aqueous phase complexing agent. The maximum achieved $SF_{Am/Cm}$ value was 6.5. For the same system without a water-soluble ligand, the separation factor values were in the range of 1.7–1.9. The concentration of nitric acid in these experiments was 0.2 M. Increasing the nitric acid concentration in the aqueous phase suppressed the extraction of metal cations as the distribution ratios of Am(III) and Cm(III) became lower than 1 for 1 M HNO_3 .

In the case of the second system with a hydrophobic ligand DOODA (C12) (Figure 6b), the $SF_{Am/Cm}$ reached a maximum value of 2.45 at a nitric acid concentration of 5 M where the distribution ratios of Am and Cm were reported to be 4.9 and 2.0, respectively. At a lower concentration of nitric acid, the distribution ratios became significantly lower.

Combination of the aforementioned ADAAM(EH) ligand (Figure 2) and TEDGA (Figure 5) resulted in an unprecedented $SF_{Am/Cm}$ value of 41.^[65] However, the values of the americium and curium distribution ratios of 0.3 and 0.0073, respectively, were found to be too small to separate them under these conditions, at least without changing the ratio of the volumes of the contacting phases.

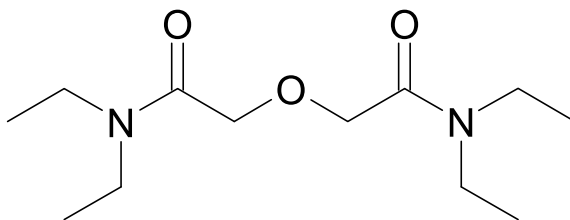


Figure 5. Structure of *N,N,N',N'*-tetraethyldiglycolamide (TEDGA).

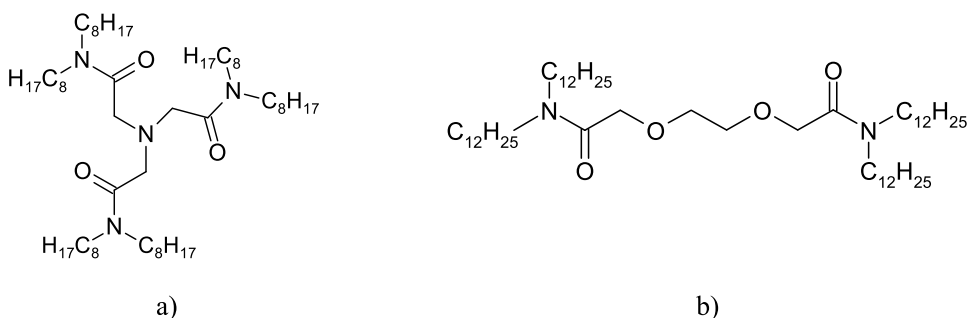


Figure 6. Structural formulae of (a) NTAamide and (b) DOODA(C12) ligands.

The most studied extraction systems with a water-soluble ligand TEDGA or its analogues are based on a malonamide (DMDOHEMA) and HDEHP (Figure 7) in TPH as in the EXAm process (vide infra). In the works,^[83,84] analogues of TEDGA containing various substituents at the amide nitrogen atom (methyl, *n*-propyl, *n*-butyl, iso-propyl, iso-butyl, 1-methylbutyl) were considered and the highest selectivity was obtained for TEDGA with an $SF_{Am/Cm}$ value of 2.5. In the case of methyl and *n*-propyl substituted diglycolamides (DGA), the $SF_{Am/Cm}$ values were lower at 1.8 and 1.1, respectively.^[65] Though the ligands with larger substituents, viz. *n*-butyl – were hydrophobic and were considered as extractants in a solution of 1-octanol and hydrogenated tetrapropylene (TPH), the $SF_{Am/Cm}$ values in such cases did not exceed 1.5.

In addition to shedding light on the effect of the structure of the water-soluble ligand on the distribution ratios and SF values, it was shown^[83] that TEDGA could be extracted both in its uncomplexed form and also as part of metal complexes from nitric acid medium with active involvement of DMDOHEMA. It was also important to note that only complexes with An/Ln:TEDGA ratios of 1:1 and 1:2 were extracted into the organic phase while the 1:3 complexes were not extracted.^[84] On the basis of thermodynamic modeling, the authors suggested that the reason for the higher extractability of americium in comparison with curium was the formation of TEDGA complexes of different composition: complexes with the stoichiometry of 1:1 and 1:2 are formed in the case of americium, and only 1:2 in the case of curium.^[85] Thus, the effect of the

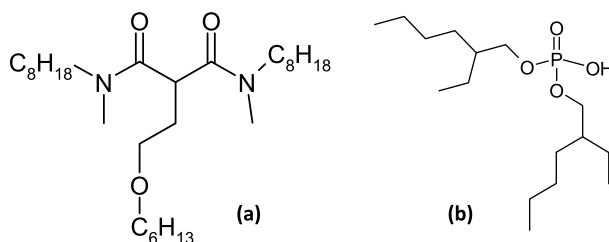


Figure 7. Structures of (a) *N,N'*-dimethyl-*N,N'*-dioctyl-2-(hexyloxy)ethylmalonamide (DMDOHEMA) and (b) di-2-ethylhexyl phosphoric acid (HDEHP).

TEDGA presence is not only limited to the stronger bonding and retention of curium in the aqueous phase, but also to the formation of different complexes in the organic phase. Formation of mixed DMDOHEMA-TEDGA complexes with Cm(III) was also observed in^[86] by TRLIFS as well as decreasing of binding ability of TEDGA with additional methyl-groups. TEDGA alone has reported to have shown preference for Cm(III) over Am(III) ($SF_{Cm/Am} = 2.6$) when extracted from 3 M HNO₃ using a 10 mM solution of the ligand in C₄mim.Tf₂N, an ionic liquid.^[87] While an extraction chromatographic resin was prepared to yield $SF_{Cm/Am}$ value of 14 at 0.1 M HNO₃, the D values were found to be too high for any effective separation. Influence of the TEDGA ligand was also investigated for extraction by CyMe₄BTPPhen ligand.^[88] It was shown that $SF_{Am/Cm}$ values increased from 1.8 in the case where only CyMe₄BTPPhen was used to 2.3–4.9 for the mixture of CyMe₄BTPPhen and TEDGA in the experiments carried out with trace amounts of Am(III) and Cm(III). The highest $SF_{Am/Cm}$ value was achieved in dilute nitric acid in the concentration range of 0.03–0.5 M. However, the increase in the concentration of the metal ions resulted in a decrease in the separation factor. Separation factor for Am/Cm of up to 3.9 was achieved for this system with a solvent containing the nitrate form of Aliquat 336 as the ionic liquid diluent and CyMe₄BTPPhen as the extracting ligand for trace amounts Am and Cm.^[89]

Extraction systems with preferential extraction of Cm(III)

Most of these systems are represented by *N,N,N',N'*-tetra-*n*-octyl diglicolamide (TODGA) as an extractant. This extractant has no pronounced selectivity for trivalent actinides in the presence of lanthanides and it also can efficiently extract some fission products such as, Zr(IV) and Pd(II).^[48] However, extraction and separation of Am and Cm can be achieved by selective stripping with water-soluble ligands. Water-soluble ligands, which improve the separation of the americium-curium pair, can also allow separation of americium from HLW in a single extraction process.

Hydrophilized bistriazines of *N*-heterocycles

The aforementioned bis-triazinyls of *N*-heterocycles were modified into water-soluble compounds and tested in systems containing TODGA as an extractant. Their transformation into water-soluble ligands was performed by introducing phenyl substituents with sulphonate groups into the triazine moieties. The following are the tetra-sulphonated bis-triazinyl *N*-heterocyclic ligands: A) SO₃-Ph-BTP – the analogue of bis-triazinyls of pyridine; B) SO₃-Ph-BTBP – the analog of bis-triazinyls of bipyridine; C) SO₃-Ph-BTPPhen – the analogue of bis-triazinyls of phenanthroline^[90–95](Figure 8).

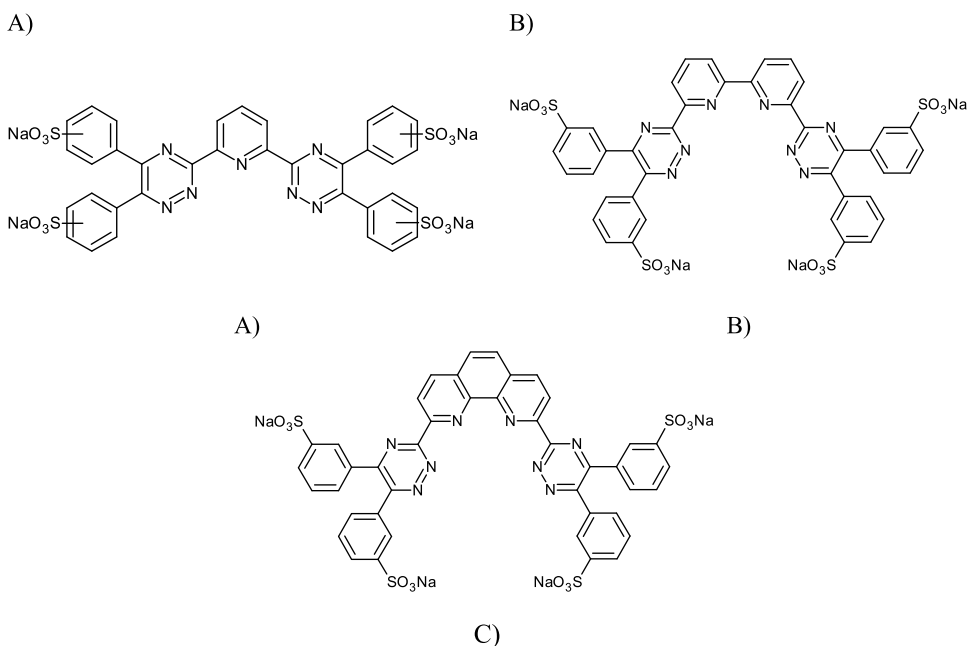


Figure 8. Structural formulae of the sulfonated ligands: A) $\text{SO}_3\text{-Ph-BTP}$; B) $\text{SO}_3\text{-Ph-BTBp}$; C) $\text{SO}_3\text{-Ph-BTPhen}$.

The main extraction parameters with respect to Am(III) and Cm(III) are given in Table 4 for systems with 0.2 M TODGA solution in hydrogenated tetrapropylene (TPH) with the addition of 5% 1-octanol as an extractant.

The water-soluble derivative of bis-triazinyl pyridine, 2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazine-3-yl)pyridine ($\text{SO}_3\text{-Ph-BTP}$, Figure 8a), was previously proposed for the selective extraction of actinides(III) in an *i*-SANEX^[96] and EURO-GANEX^[97] processes. In these processes, actinides were first co-extracted with the REEs by TODGA with subsequent selective stripping of actinides with the water-soluble ligand solution. However, application of aqueous solution of the $\text{SO}_3\text{-Ph-BTP}$ doesn't allow separation of americium and curium – distribution ratios of Am(III) and Cm(III) are practically equal.

In the case of the bipyridine derivative ($\text{SO}_3\text{-Ph-BTBp}$), an increase in the $\text{SF}_{\text{Cm}/\text{Am}}$ values depended on the concentration of the feed nitric acid. The

Table 4. Comparison of Am/Cm extraction/separation behavior using water-soluble ligand based on bis-triazine *N*-heterocycle. Organic phase: 0.2 M TODGA in TPH.

Parameter	Water-soluble ligand		
	$\text{SO}_3\text{-Ph-BTP}^{[91]}$	$\text{SO}_3\text{-Ph-BTBp}^{[92]}$	$\text{SO}_3\text{-Ph-BTPhen}^{[93]}$
D_{Cm}	0.01–20	$1.5 \cdot 10^{-3}$ –20	$2.3 \cdot 10^{-3}$ –10
D_{Am}		$5 \cdot 10^{-4}$ –8	$5 \cdot 10^{-3}$ –5
$\text{SF}_{\text{Cm}/\text{Am}}$	≈ 1	2.4–3.6	2.5–4.5
$c(\text{HNO}_3)$, M	0.1–1	0.2–1.5	0.01–1

values varied in the range from 2.4 to 3.6. At the optimal concentration of nitric acid, when $D_{\text{Cm}} > 1$ and $D_{\text{Am}} < 1$, the $SF_{\text{Cm/Am}}$ value was 2.5 whereas the $SF_{\text{Eu/Am}}$ value was ca. 120. The AmSel (Americium Selective Extraction)^[92] process was developed in 2015 on the basis of an *i*-SANEX process. The AmSel process allowed selective extraction of americium using 0.2 M TODGA in Exxsol D80 containing 5% (vol.) 1-octanol as the organic phase and 0.02 M solution of $\text{SO}_3\text{-Ph-BTBP}$ in dilute nitric acid.

The similar phenanthroline-based ligand ($\text{SO}_3\text{-Ph-BTPhen}$) demonstrated a close selectivity to americium, which leads to an even greater increase in the $SF_{\text{Cm/Am}}$ values.^[93] The achieved $SF_{\text{Cm/Am}}$ values were in the range of 2.4–3.6 while the $SF_{\text{Eu/Am}}$ value was ca. 600 after stripping the metal ions from the organic phase (0.2 M TODGA + 5 vol.%, 1-octanol in the hydrocarbon diluent Exxsol D80) with a solution of 20 mM $\text{SO}_3\text{-Ph-BTPhen}$ + 0.5 M HNO_3 . The separation factor for americium and the closest in chemical properties rare earth element – lanthanum was ca. 20.

As seen with TEDGA, the addition of the water-soluble phenyl sulfonated ligand could lead to the formation of mixed extracted species in the organic phase. Search for mixed complexes in TODGA- $\text{SO}_3\text{-Ph-BTP/SO}_3\text{-Ph-BTBP}$ systems showed only homoleptic species in both phases. However, mixed complexes existing in the case of monophasic systems of TEDGA and the sulfonated ligands^[94] indicated the possibility of the formation of mixed complexes between the organic soluble BTP and BTBP with TEDGA.

The studies^[78,98] describe the effect of bis-phenylsulfonate-derivatives of BTP and BTBP on the extraction of Am-Cm (Figure 9). The absence of two meta-sulpho-phenyl group in the ligand structures resulted in the vanishing the effect of these ligands on the metal ion extraction by 0.2 M TODGA in 1-octanol/kerosene (5:95). The authors explained this phenomenon by the greater solubility of the americium complexes with the corresponding tetra-sulfonate-derivative.

Thus, among the presented water-soluble ligands, the most promising in terms of selectivity towards Am(III) is the $\text{SO}_3\text{-Ph-BTPhen}$. However, this class of ligands does not satisfy the CHON principle. The detachment of sulfonate group due to radiolysis will lead to the release of sulfate-anion into the radioactive waste, and will likely to lead to lower solubility of the ligand in the aqueous phase.

Polyamino acidic complexation agents (various complexation agents)

The only example of increasing selectivity in the separation of americium and curium by using the aza-crown ring is presented in the study^[99] of water the soluble N,N' -bis[(6-carboxy-2-pyridyl)methyl]-1,10-diaza-18-crown-6 ($\text{H}_2\text{BP18C6}$) (Figure 10). It was shown that $\text{H}_2\text{BP18C6}$ formed a more stable complex with americium (III) which has a larger ionic radius than that of curium (III). The ratio of the complex formation constants for americium and

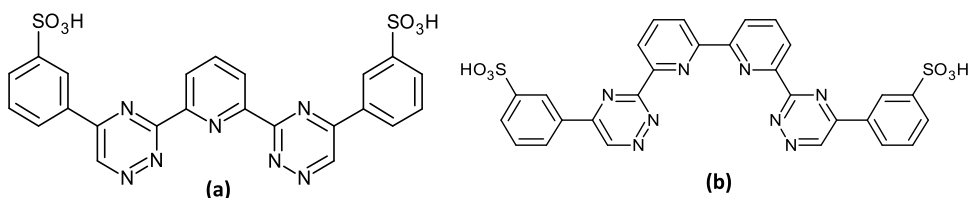


Figure 9. Structural formulae of (a) bis-phenylsulfonate-derivatives of BTP and (b) BTBP^[78,98].

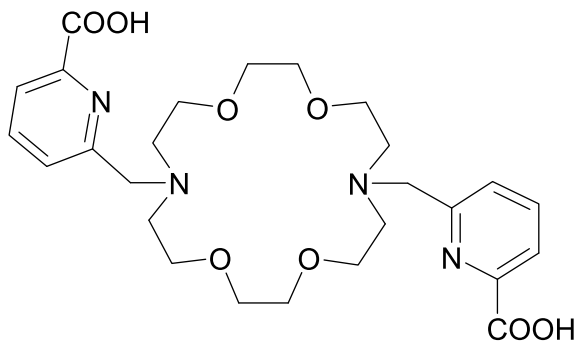


Figure 10. Structural formula of *N,N'*-bis[(6-carboxy-2-pyridyl)methyl]-1,10-diaza-18-crown-6 (H2BP18C6).

curium is equal to 4.1. Addition of this ligand into the extraction system “0.001 M HDEHP in orthoxylene” resulted in a higher value of $SF_{Cm/Am}$ (ca. 6.5) at pH = 3. DFT calculations showed that the steric constraints of the diaza-crown ring are the main factor affecting the selectivity.

In a subsequent study, H2BP18C6 was tested as an alternative to the poly-amino carboxylic acids (e.g., DTPA, HEDTA, etc) used in the TALSPEAK and ALSEP processes.^[100] The researchers studied the distribution of Am(III), Cm(III) and Ln(III) into organic phases containing di-2-ethylhexyl phosphoric acid (HDEHP) or mono-2-ethylhexyl ester of 2-ethylhexyl phosphonic acid (HEH[EHP]) in ortho-xylene from the aqueous phase containing H2BP18C6, sodium nitrate (salting out agent) and lactate buffer (pH \approx 3). Under these conditions, americium was separated from curium and lanthanides heavier than praseodymium though the same was not possible from the light lanthanides – lanthanum, cerium and partially praseodymium. However, relatively high selectivity in the separation of lanthanides was observed: the extraction constants in the series from lanthanum to lutetium increased by 8 orders of magnitude.

Borriniet al.^[101] studied the effect of water-soluble ligands based on pyridine dicarboxylic acid and *N,N,N',N'*-tetrakis-[(6-carboxypyridin-2-yl)-ethylene diamine (H4TPAEN) (Figure 11a) on the extraction of americium(III), curium(III) and europium(III) by TODGA. No significant effect on the separation of

the curium-amerium pair in the case of derivatives of pyridinedicarboxylic acid (PDCA, [Figure 11b](#)) have been established, whereas the addition of H4TPAEN into the aqueous phase increased the separation factor $SF_{\text{Cm/Am}}$ values to 3.3–4.5 depending on the nitric acid concentration and ionic strength (adjusted using NaNO_3). The disadvantage of the latter ligand is its low solubility in nitric acid solutions (up to 5 mM). H4TPAEN demonstrates also low selectivity in separating americium from light lanthanides – lanthanum and cerium, which is very sensitive to ligand and lanthanides concentration, and temperature. For example, separation of americium from the light lanthanides was not possible at H4TPAEN concentrations of 0.0025 M and 0.0025 M lanthanides (about 0.4 g/L). The separation factors of the light lanthanides and americium increased at the ligand concentration above 0.0025 M, but such solutions are unstable due to the low solubility of H4TPAEN at $\text{pH} = 1$. The main problems that can arise during the dynamic testing of the TODGA/H4TPAEN extraction system and methods to overcome them are considered in the published literature.^[56,102]

A systematic study of the effect of structural modifications of H4TPAEN ligand on its complexing properties is presented in the studies carried out by Gracia et al.^[103] The authors synthesized 9 ligands ([Figure 12](#)) and investigated their effect on the back extraction of Am/Cm from organic phases of two compositions: a) 0.3 M HDEHP/0.6 M DMDOHEMA (extractant used in the EXAm process), b) 0.2 M TODGA/0.5 M TBP with TPH as the diluent for both the extraction systems. These two organic phases were selected, because the first mixture extracts americium and light lanthanides more effectively while the second one does so for curium and heavy lanthanides. All the new water-soluble ligands demonstrated the lower selectivity in the separation of americium and curium than H4TPAEN. The closest selectivity to the starting ligand has L6 ligand ($SF_{\text{Cm/Am}}$ value of 2.7 versus 3.1) with additional methoxy-groups in pyridine rings. The main advantage of the new group of ligands is their higher solubility (L9 is an exception) – at least 5 mM at $\text{pH} = 1.5$ versus 1 mM for H4TPAEN. A surprising observation in the TODGA/TBP system was the higher distribution ratio of Am(III) in the presence of water-soluble

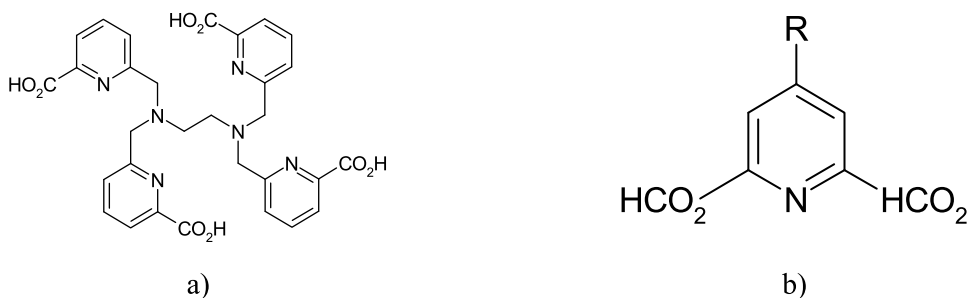


Figure 11. Structural formula of (a) H₄TPAEN and (b) general structure of 2,6-pyridine-dicarboxylic acids ($R = \text{H}, -\text{CH}_2\text{OH}, -\text{C}_2\text{H}_5, -\text{C}(\text{O})\text{C}_2\text{H}_5, -\text{CO}_2\text{H}, -\text{OCH}_3, \text{Cl}$).

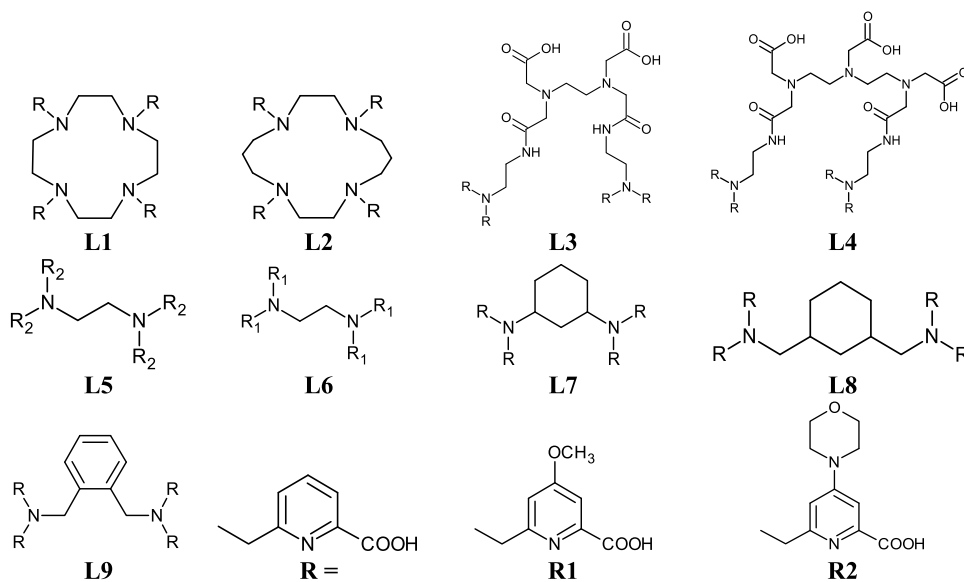


Figure 12. Modified structures of H4TPAEN ligand studied for Am/Cm separation.^[103]

ligands L1, L2, L5, L7-L9 than without them. The authors suggested that this effect is associated with the solubility of the formed complexes in the organic phase, but they did not confirm this experimentally. Structures of the complexes of Am(III)/Cm(III) and H4TPAEN ligand were studied in two separate studies.^[104,105] It was shown, that americium position is slightly deeper in the pseudo-cavity of this ligand than that of curium. The authors explained the difference in the binding strength by competition between the nitrogen and oxygen atoms, and by small structural differences.

A precursor of H4TPAEN ligand (Figure 11) without the carboxyl groups – TPAEN ligand – was studied earlier in,^[106] where the constants of complex formation with Am(III), Sm(III), and La(III) were determined by potentiometric titration. A comparison of the constants for TPAEN and H4TPAEN ligands is presented in Table 5. Despite the different experimental conditions, it can be noted that the introduction of the carboxyl groups significantly reduced the difference in the complex formation constants for lanthanum and samarium, but did not significantly affect the selectivity of Am/Ln separation.

Sasaki et al.^[107] studied an extraction system based on *N,N,N',N'*-tetra-*n*-dodecyl diglycolamide (Figure 13a) and the water-soluble ligand DOODA (C2) – *N,N,N',N'*-tetraethyl-3,6-dioxaoctanediamide (analogue of Figure 6b). An $SF_{Cm/Am}$ value of 3.3 was achieved at 3 M nitric acid and 0.2 M DOODA (C2) concentrations in the aqueous phases.

Another interesting result has been shown for 3,4,3-LI-(1,2-HOPO)^[108–110] ligand (Figure 13b). Despite that the main feature of this ligand being a very strong complexation with An(IV) cations, $\log\beta$ values for Am and Cm differ

Table 5. Conditional constants of complex formation ($\log \beta$) for 1:1 complexes of H4TPAEN and TPAEN ligands with Am(III), Cm(III), La(III) and Sm(III) at 25°C. Conditions: 0.1 M of HNO_3 in the case of H4TPAEN ligand, 0.1 M NaClO_4 in the case of TPAEN ligand. Methods: H4TPAEN – microcalorimetric titration (La and Sm) and UV-Vis titration (Am), Time-Resolved Laser Fluorescence Spectroscopy (Cm); TPAEN – potentiometric titration.

Metal	H ₄ TPAEN ($\log \beta$) ^[104]	TPAEN ($\log \beta$) ^[106]
Am	4.5 ± 0.2	6.77 ± 0.01
Cm	4.3 ± 0.2	-
La	2.8 ± 0.1	3.52 ± 0.02
Sm	3.0 ± 0.1	4.70 ± 0.02

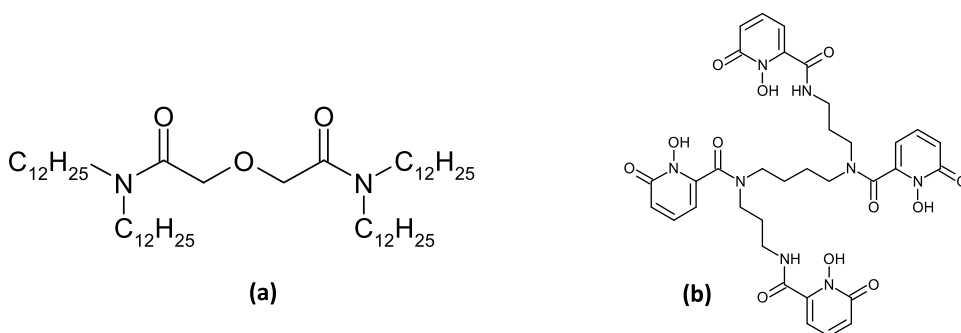


Figure 13. Structures of (a) *N,N,N',N'*-tetra-*n*-dodecyl diglycolamide and (b) 3,4-LI-(1,2-HOPO).

by two orders of magnitude. Together with its ability to form complexes in highly acidic media (1–10 M H^+) it makes this ligand is very promising for the metal ion separations.

The extraction systems for Am(III) and Cm(III) separation tested in dynamic modes

Even with high separation factors, a pure americium product can be obtained only if it is deployed in a multi-step counter-current process. The higher the separation factor, the fewer steps in the cascade of extractors will be needed to achieve the necessary purity and the overall yield of the product.

The dynamic experiments show the reproducibility of distribution ratios, separation factors, and stability of streams. In these tests, the initial solutions usually simulate the composition of HLW and step by step go to the real ones. At the very first stage, trace amounts of radionuclides are used, and stable isotopes are for all elements that have them.

DMDOHEMA process

The extraction system based on the malonamide, DMDOHEMA (Figure 7) was tested in a dynamic mode with weighed quantities of americium (155 mg/L) and

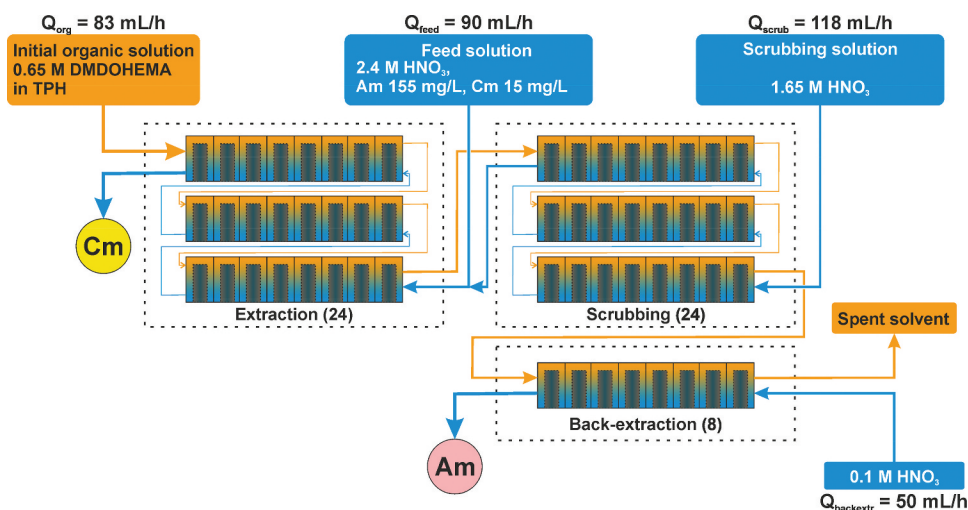


Figure 14. Flow sheet of DMDOHEMA process. The number of stages is given in brackets.

curium (15 mg/L).^[55] The principal flow-sheet of the system is presented in Figure 14. The process consisted of 56 stages: 24 – extraction, 24 – scrubbing, 8 – back-extraction.

Separation factor ($SF_{Am/Cm}$) of 1.5 was achieved in the tested system. The final product of americium contained 0.7% of the curium inventory while the curium product contained 0.6% of the americium inventory. The authors mentioned hydrodynamic problems during Am stripping. This process is a good example of the difficulty of separating an americium-curium pair using an extraction system with a separation factor of 1.5. This also demanded the development of more efficient processes.

LUCA process

The flow-sheet of the LUCA process tested in a dynamic mode with centrifugal extractors is presented in Figure 15.^[111] The initial solution contained trace amounts of americium-241, curium-244, europium-152, and californium-252 spiked in 0.084 M nitric acid and 0.5 M sodium nitrate. The high separation factor allowed the efficient separation of americium and curium in just 16 stages of extraction/scrubbing. The purity of americium was 99.53%, and the decontamination factor was > 1000 .

This extraction system has the following disadvantages. The organic phase does not meet the CHON principle and the secondary waste can contain sulfates and phosphates arising from solvent clean-up which can significantly enhance the waste volume and lead to difficulty in fixing into a solid matrix. The presence of sulfur atoms leads to poor radiolytic and hydrolytic stability of the extractant. The sulfate anion formed under these conditions has limited

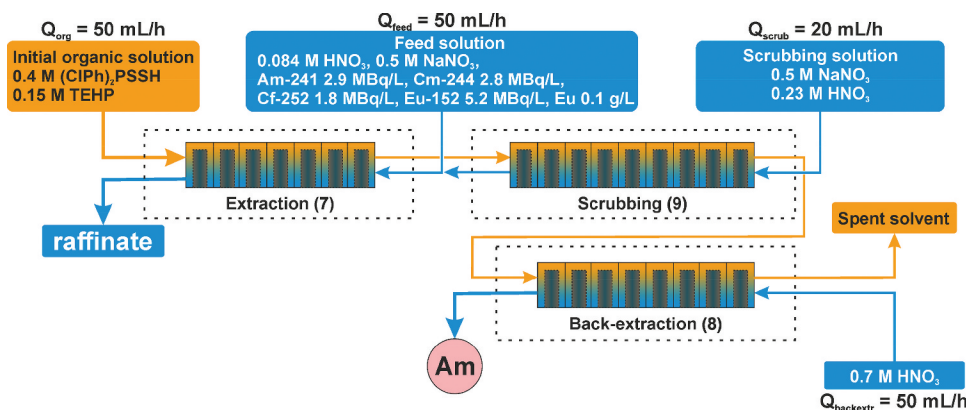


Figure 15. Flow sheet of the 24 stage LUCA process. The number of stages is given in brackets.

solubility in a glass matrix used for waste immobilization.^[112] As a result, the industrial application of this system appears remote.

ADAAM process

The aliphatic diamide amine ADAAM(EH) (Figure 2) was tested in a dynamic mode (Figure 16) for the separation of americium(III) and curium(III).^[63]

Preliminary results demonstrated that the optimal separation factor was obtained at a nitric acid concentration of 1.5 M. The equilibrium in the system established within 20 seconds for extraction and within 90 seconds (shaker speed of 240 rpm) for back extraction.

Dynamic tests were performed with trace amounts of radionuclides – specific activities were 10 kBq/mL for americium-241 and 4.7 kBq/mL for curium-244 (Table 6). The counter-current setup consisted of 32 mixer-settler stages, 8 extraction stages, 8 scrubbing stages, and 16 stripping stages (see Figure 16).

EXAm process

The most developed process for extraction of americium directly from PUREX raffinates is the EXAm (*Extraction of Americium*) process. This process and its extraction chemistry was recently reviewed.^[22] The first test of the separation of americium from surrogate raffinates of the PUREX process was performed in the ATALANTE laboratory (France) in 2010.^[113] The flow-sheet of the EXAm process^[22] is presented in Figure 17. The key idea of the process is to increase the separation factor of the americium-curium pair by the addition of the water-soluble ligand, TEDGA. The separation factor of this pair is 1.6 for the extraction system based on a mixture of *N,N'*-dimethyl-*N,N'*-dioctyl-2(hexyloxy)ethyl malonamide and

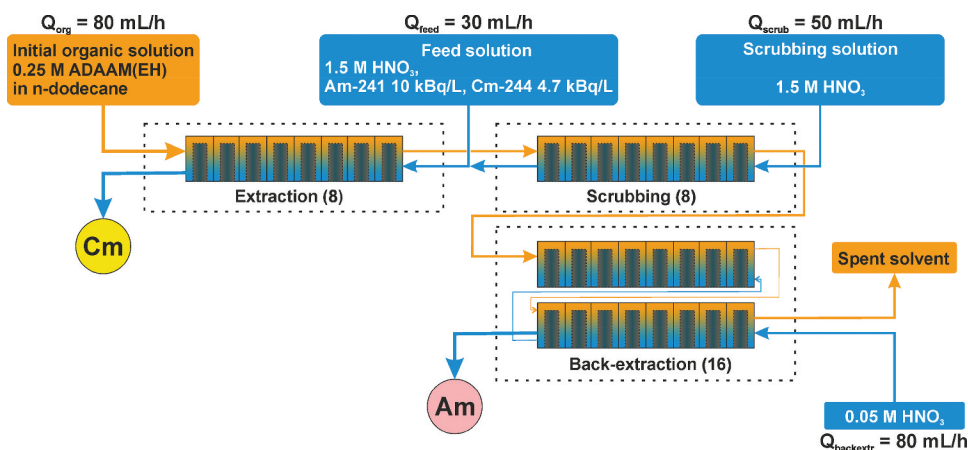


Figure 16. Flow-sheet of the ADAAM process. The number of stages is given in brackets.

Table 6. Compositions of the obtained products of ADAAM process.

Radionuclide	Activity and fraction of activity in the initial solution, kBq/mL (%)	
	Am product	Cm product
Am-241	9.98 (99.8)	0.02 (0.2)
Cm-244	0.45 (9.6)	4.23 (90)
Am-241, %a	99.8	53.9
Cm-244, %a	0.2	46.1
Am/Cm	525	1

a mass fractions are recalculated from data on activity of Am-241 and Cm-244

HDEHP (Figure 7). The $SF_{Am/Cm}$ value was found to increase to 2.5 in the presence of TEDGA, which allowed the separation of the Am/Cm pair in 32 stages of extraction/scrubbing.

The compositions of the solutions at different stages of this process are presented in Table 7. The feed solution contains TEDGA ligand.

The next step is scrubbing (0.5 M citric acid, pH = 3) the extracted molybdenum from the organic phase where a part of americium (0.7%) is lost. The separation of americium from light lanthanides is performed at the stage of selective back extraction with a solution of 0.5 M HEDTA in 0.5 M citrate buffer (pH = 3). Then the organic phase is regenerated by the back extraction (0.2 M TEDGA, 0.5 M oxalic acid, 1 M HNO₃) of light lanthanides and iron.

The main disadvantage of the EXAm process is the high tendency of the extraction system to extract light lanthanides. This problem is solved by selective scrubbing, but the product of americium is still contaminated with neodymium (2.2% of Nd in mass/Am mass), and the yield of extraction of americium is 98.3%. The separation factor of the americium-curium pair is not high (2.5), resulting in 68 steps of the counter-current process in total. The achieved decontamination factor for Am against Cm was 500.

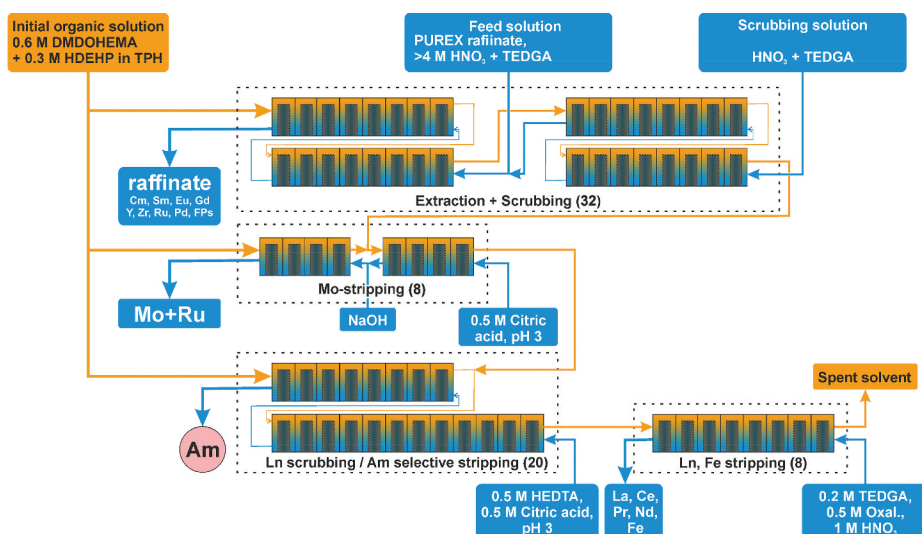


Figure 17. Flow-sheet of ExAm process hot test in 2010. The number of stages is given in brackets. Oxal = oxalic acid.

Table 7. The composition of the solutions at different stages of EXAm process (hot test in 2010)^[113].

Element	Feed solution, mg/L	Raffinate, mg/L	Mo scrub, mg/L	Am product, mg/L	Ln scrub, mg/L	Balance, %	Decontamination factor
Am	220	0.79	0.62	566	0.018	105	
Cm	21.6	10.5	0.0002	0.11	0.0033	136	505
Ce	573	<1	<5	<2.5	960	75	>585
Nd	1650	3.7	<5	12.5	2350	113	340
Eu	60	21	<2.5	<2.5	<5	98	>61
Gd	83	30	<2.5	<2.5	<5	101	>85
Mo	1000	<1	420	<5	<5	105	>510
Zr	890	290	<2.5	<5	110	101	>458
Pd	550	<1	190	115	<5	95	12

In 2015, americium was extracted directly from concentrated PUREX raffinate.^[114] In comparison with 2010, the system was modified to handle higher amounts of radionuclides, and the main differences were: a) the additional 4 stages with TEDGA scrubbing, b) Am stripping was performed with DTPA + malonic acid instead of HEDTA + citric acid. Although a mode with a lower yield of americium extraction was used to obtain americium with higher purity, the product contained 2.4 g of Am contaminated with 0.6% curium, 1.7% lanthanides, 0.3% iron, 0.05% molybdenum, 0.7% palladium, and 1.1% ruthenium (Table 8). The authors noted that the DF Am/Cm was lower than expected and needs to be improved. This improvement can be done by increasing number of stages in Cm-scrubbing section by 24 additional steps.

Table 8. The composition of the initial and Am-product solutions at different stages of ExAm process (hot test in 2015)^[22].

Element,	Feed solution, mg/L	Am-product, mg/L	Relative concentration in Am product, %
Am	1095	884	82
Cm	323	5.3	0.6
La	1245	<0.05	1.8
Ce	2169	2.1	-
Pr	956	1.4	-
Nd	3269	13.2	-
Sm	917	<0.05	-
Eu	151	-	-
Gd	376	-	-
Y	129	-	-
Zr	900	0.05	-
Mo	1193	0.47	0.05
Fe	122	2.7	0.3
Pd	617	6.3	0.7
Ru	1472	9.9	1.1

Despite the large numbers of stages and process steps, the EXAm process is currently the only extraction process for selective Am isolation tested on concentrated PUREX-raffinate.

Comparison of the processes

The general overview of the aforementioned processes is given in Table 9. One can see a huge difference in the decontamination factor and Am recovery between tests with trace and macro amounts of radionuclides.

Out of the processes, ADAAM process is promising for hot tests due to high SF values and satisfaction to CHON-principle, but there is still no information on radiation stability of this ligand.

Conclusions and perspectives

We have reviewed the existing solvent extraction systems for the separation of the americium (III)-curium (III) pair from nitric acid solutions without redox reactions. Though a significant number of literature reports are available on the lab-scale separation studies using radiotracers, only very few of such systems are tested in counter-current mode suggesting the difficulty in the separation of these elements.

Studies on the An(III)/Ln(III) separations resulted in a wide variety of extractants containing soft binding centers – aromatic nitrogen atoms or sulfur atoms (bistriazinyl pyridines, bistriazinyl bipyridines, bistriazinyl-phenanthroline, thio-phosphinic acids) – with reasonably high separation factors ($SF_{Am/Ln} \approx 50-100$). Due to the high similarity in the chemical properties of Am(III) and Cm(III) their difference cannot be predicted by the Pearson's HSAB theory. This makes the search routes for the selective extractant very obscure. That is the reason why only a small number of individual extractants or extraction systems with $SF_{Am/Cm}$ values higher than 1.5 are proposed. And the reasons for the higher selectivity of

Table 9. Overview of dynamical processes for Am-Cm separation. DF – decontamination factor, HAC – high active concentrate.

Process	DMDOHEMA	EXAm 2010	EXAm 2015	ADAAM	LUCA
SF _{Am/Cm}	1.5	2.5	2.5 (1.8)a	6	8
Number of stages for Am/Cm separation	48	32	32	16	16
Initial feed	Am (0.155 g/L) +Cm (0.015 g/L) in HNO ₃	Am (0.2 g/L)+Cm (0.3 g/L) in surrogate raffinate	Am (1.1 g/L)+Cm (0.3 g/L) in HAC	Spike amounts in HNO ₃	Spike amounts in NaNO ₃ and HNO ₃
DF	-	500	50	10	>1000
Am recovery, %	99.4	98	82	99.8	98.9–103.3

a– estimated from flowsheet modeling

a certain system are not yet clear. An increase in the selectivity can be associated with various changes in the structure of ligands resulting, for example, in different sizes of potential “cavities” for cations. Different research groups made general statements about effects of a decrease in the effective charge, changes in the energies of the HOMO and LUMO, etc. But the specific factors that define the selectivity are not given in the literature. That is true also for the studies on the water-soluble ligand H4TPAEN.^[101,103,105] Extensive studies of “structure – property” dependences, modeling of the structures of complexes, and analysis of chemical bonds between metal cations and organic molecules allow only comparing the theoretical calculations with the observed selectivity, but not predicting it.

One of the possible approaches may be the search among ligands forming supramolecular structures, as was shown, for example, in the separation of neighboring lanthanides.^[115] But application of such systems in industry requires additional studies.

Another approach can be based on a “kinetic” effect, as has been shown for bis-triazinyl-phenanthroline derivatives. Previously, a long time for reaching equilibrium in systems based on bis-triazinyls of *N*-heterocycles was considered as a disadvantage.^[116,117] But in fact, it was exactly the factor that allowed increasing the $SF_{Am/Cm}$ values due to different extraction rates of americium and curium. Considering that the impeller speed is very high in mixer-settler systems the kinetic factors may become redundant. However, this type of extractor is not optimal for radiochemical application from absorbed dose point of view. So further development of such process requires investigation of extraction rates in centrifugal contactors.

One of the most promising technological solutions for the separation of the Am-Cm pair is the application of water-soluble ligands in processes viz. AmSel, EXAm, 1-cycle SAmEX and TODGA-H4TPAEN. However, water-soluble ligands are not considered for multiple uses. Thus, the requirements for their radiolytic and/or hydrolytic stability are not so stringent, but the question of meeting the CHON-principle is acute. But still, the $SF_{Am/Cm}$ values in these systems are not high (<4) and depend on many factors. This can lead to difficulties and low decontamination factors of americium during its extraction and separation from solutions of real high-level waste or similar solutions, as noted by the authors of the EXAm process.^[114] From a fundamental point of view, the possibility of formation of mixed complexes is important for any new extraction system.

This review demonstrates that the search of the extraction system for efficient separation of the americium-curium pair is far from its finish line. We hope that this work will attract scientific attention of new research groups that will help to find the solution.

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References

- [1] Myasoedov, B. F.; Kalmykov, S. N. Nuclear Power Industry and the Environment. *Mendeleev Commun.* **2015**, 25(5), 319–328. DOI: [10.1016/j.mencom.2015.09.001](https://doi.org/10.1016/j.mencom.2015.09.001).
- [2] Healy, T. V. The Reaction of Nitric Acid with Formaldehyde and with Formic Acid and Its Application to the Removal of Nitric Acid from Mixtures. *J. Appl. Chem.* **1958**, 8(9), 553–561. DOI: [10.1002/jctb.5010080903](https://doi.org/10.1002/jctb.5010080903).
- [3] Choppin, G.; Liljenzin, J.-O.; Rydberg, J. Ekberg Christian. In *Radiochemistry and Nuclear Chemistry*. 4th ed.; Academic Press, New York, **2013**; 866 p.
- [4] Alyapyshev, M. Y.; Babain, V. A.; Ustynyuk, Y. A. Recovery of Minor Actinides from High-Level Wastes: Modern Trends. *Russ. Chem. Rev.* **2016**, 85(9), 943–961. DOI: [10.1070/RCR4589](https://doi.org/10.1070/RCR4589).
- [5] Bohr, N.; Wheeler, J. A. The Mechanism of Nuclear Fission. *Phys. Rev.* **1939**, 56, 426–450. DOI: [10.1103/PhysRev.56.426](https://doi.org/10.1103/PhysRev.56.426).
- [6] Frugier, P.; Roudil, D.; Peugeot, S.; Broudic, V.; Je, C.; Deschanel, X.; Rabiller, H.; Noel, P. Y. Effect of Alpha Radiation on the Leaching Behaviour of Nuclear Glass. *J. Nucl. Mater.* **2007**, 362, 474–479. DOI: [10.1016/j.jnucmat.2007.01.099](https://doi.org/10.1016/j.jnucmat.2007.01.099).
- [7] Tribet, M.; Rolland, S.; Peugeot, S.; Broudic, V. Irradiation Impact on the Leaching Behavior of HLW Glasses. *Procedia Mater. Sci.* **2014**, 7, 209–215. DOI: [10.1016/j.mspro.2014.10.027](https://doi.org/10.1016/j.mspro.2014.10.027).
- [8] Poinssot, C.; Rostaing, C.; Baron, P.; Warin, D. Main Results of the French Program on Partitioning of Minor Actinides, a Significant Improvement Towards Nuclear Waste Reduction. *Procedia Chem.* **2012**, 7, 358–366. DOI: [10.1016/j.proche.2012.10.056](https://doi.org/10.1016/j.proche.2012.10.056).
- [9] United States Environmental Protection Agency. RADInfo Glossary of Radiation Terms.
- [10] Wang, H.; Otsu, H.; Sakurai, H.; Ahn, D. S.; Aikawa, M.; Doornenbal, P.; Fukuda, N.; Isobe, T.; Kawakami, S.; Koyama, S.; et al. Spallation Reaction Study for Fission Products in Nuclear Waste: Cross Section Measurements for Cs-137 and Sr-90 on Proton and Deuteron. *Phys. Lett. B.* **2016**, 754, 104–108. DOI: [10.1016/j.physletb.2015.12.078](https://doi.org/10.1016/j.physletb.2015.12.078).
- [11] Tananaev, I. G.; Myasoedov, B. F. Commercial Recovery of Valuable Radionuclides from Spent Nuclear Fuel: Methods and Approaches. *Radiochemistry.* **2016**, 58(3), 257–264. DOI: [10.1134/S1066362216030061](https://doi.org/10.1134/S1066362216030061).
- [12] Marivoet, J.; Milot, J.-F.; Salvatores, M.; Saturnin, A.; Zaetta, A.; Geckeis, H.; Gompper, K.; Oigawa, H.; TAIWO, T. A.; Wigeland, R.; et al. *Potential Benefits and Impacts of Advanced Nuclear Fuel Cycles with Actinide Partitioning and Transmutation*. OECD PUBLISHING: Paris; **2011**, Vol. 2.

- [13] Gerasimov, A. S.; Zaritskaya, T. S.; Kiselev, G. V.; Myrtsyymova, L. A. Conditions of Transmutation of Plutonium, Americium, and Curium in Nuclear Facilities. *At. Energy*. **2000**, 89(2), 663–667. DOI: [10.1023/A:1011355626592](https://doi.org/10.1023/A:1011355626592).
- [14] Walker, C. T.; Nicolaou, G. Transmutation of Neptunium and Americium in a Fast Neutron. *J. Nucl. Mater.* **1995**, 218, 129–138. DOI: [10.1016/0022-3115\(94\)00649-0](https://doi.org/10.1016/0022-3115(94)00649-0).
- [15] Magill, J.; Berthou, V.; Haas, D.; Galy, J.; Schenkel, R.; Wiese, H. W.; Heusener, G.; Tommasi, J.; Impact, Y. G. Limits of Partitioning and Transmutation Scenarios on the Radiotoxicity of Actinides in Radioactive Waste. *Nucl. Energy-London*. **2003**, 42(5), 263–278.
- [16] Poinssot, C.; Bourg, S.; Ouvrier, N.; Combernoux, N.; Rostaing, C.; Vargas-gonzalez, M.; Bruno, J. Assessment of the Environmental Footprint of Nuclear Energy Systems. Comparison between Closed and Open Fuel Cycles. *Energy*. **2014**, 69, 199–211. DOI: [10.1016/j.energy.2014.02.069](https://doi.org/10.1016/j.energy.2014.02.069).
- [17] Taylor, R. J.; Gregson, C. R.; Carrott, M. J.; Mason, C.; Sarsfield, M. J. Progress Towards the Full Recovery of Neptunium in an Advanced PUREX Process. *Solvent Extr. Ion Exch.* **2013**, 31(4), 442–462. DOI: [10.1080/07366299.2013.800438](https://doi.org/10.1080/07366299.2013.800438).
- [18] Carrot, M. J.; Gregson, C. R.; Taylor, R. J. Neptunium Extraction and Stability in the GANEX Solvent: 0.2 M TODGA/0.5 M DMDOHEMA/Kerosene. *Solvent Extr. Ion Exch.* **2013**, 31(5), 463–482. DOI: [10.1080/07366299.2012.735559](https://doi.org/10.1080/07366299.2012.735559).
- [19] Sarsfield, B. M. J.; Taylor, R. J.; Maher, C. J. Neptunium (V) Disproportionation and Cation – Cation Interactions in TBP/Kerosene Solvent. *Radiochim. Acta*. **2007**, 682, 677–682.
- [20] Modolo, B. G.; Wilden, A.; Geist, A.; Magnusson, D.; Malmbeck, R. A. Review of the Demonstration of Innovative Solvent Extraction Processes for the Recovery of Trivalent Minor Actinides from PUREX Raffinate. *Radiochim. Acta*. **2012**, 725, 715–725. DOI: [10.1524/ract.2012.1962](https://doi.org/10.1524/ract.2012.1962).
- [21] Miguiditchian, M.; Vanel, V.; Marie, C.; Pacary, V.; Charbonnel, C.; Berthon, L.; Hérès, X.; Montuir, M.; Sorel, C. Americium Recovery from Highly Active PUREX Raffinate by Solvent Extraction: The EXAm Process. *A Review of 10 Years of R&D*. *Solvent Extr. Ion Exch.* **2020**, 38(4), 365–387. DOI: [10.1080/07366299.2020.1753922](https://doi.org/10.1080/07366299.2020.1753922).
- [22] Nichols, A. L.; Aldama, D. L.; Verpelli, M., *Handbook of Nuclear Data for Safeguards: Database Extensions*. International Atomic Energy Agency (INDC International Nuclear Data Committee); IAEA: Vienna, **2008**.
- [23] Gorshkov, V. K.; Ivanov, R. N.; Kukabadze, G. M.; Reformatsky, I. A. U-235 Fission Product Yields in the Rare Earth Region. *J. Nucl. Energy*. **1958**, 8(1–3)), 69–73.
- [24] Leinweber, G.; Barry, D. P.; Trbovich, M. J.; Burke, J. A.; Drindak, N. J.; Knox, H. D.; Ballard, R. V.; Block, R. C.; Danon, Y.; Severnyak, L. I. Neutron Capture and Total Cross-Section Measurements and Resonance Parameters of Gadolinium. *Nucl. Sci. Eng.* **2006**, 154(3), 261–279. DOI: [10.13182/NSE05-64](https://doi.org/10.13182/NSE05-64).
- [25] Salvatores, M.; Slessarev, I.; Ritter, G.; Fougeras, P.; Tchistiakov, A.; Youinou, G.; Zaetta, A. Long-Lived Radioactive Waste Transmutation and the Role of Accelerator Driven (Hybrid) Systems. *Nucl. Instruments Methods Phys. Res. A*. **1998**, 414, 5–20. DOI: [10.1016/S0168-9002\(98\)00522-1](https://doi.org/10.1016/S0168-9002(98)00522-1).
- [26] Stewart, J. E.; Eccleston, G. W.; Ensslin, N.; Cremers, T. L.; Foster, L. A.; Menlove, H. O.; Rinard, P. M. *Neutron-Based Measurements for Nondestructive Assay of Minor Actinides Produced in Nuclear Power Reactors*; Los Alamos National Lab.: NM (United States), **1996**.
- [27] Martin, R. C.; Knauer, J. B.; Balo, P. A. Production, Distribution and Applications of Californium-252 Neutron Sources. *Appl. Radiat. Isot.* **2000**, 53, 785–792. DOI: [10.1016/S0969-8043\(00\)00214-1](https://doi.org/10.1016/S0969-8043(00)00214-1).

- [28] Apostol, A. I.; Zsigrai, J.; Bagi, J.; Brandis, M.; Nikolov, J.; Mayer, K. Characterization of Californium Sources by Gamma Spectrometry : Relevance for Nuclear Forensics. *J. Radioanal. Nucl. Chem.* **2019**, 321(2), 405–412. DOI: [10.1007/s10967-019-06628-0](https://doi.org/10.1007/s10967-019-06628-0).
- [29] Karelin, Y. A.; Gorffev., Y. N.; Karasev, V. I.; Radchenko, V. M.; Schimbarev, Y. V.; Kuznetsov, R. A. Californium-252 Neutron Sources. *Appl. Radiat. Isot.* **2000**, 48(10), 1563–1566. DOI: [10.1016/S0969-8043\(97\)00156-5](https://doi.org/10.1016/S0969-8043(97)00156-5).
- [30] Morss, L. R.; Edelstein, N. M.; Fuger, J. *The Chemistry of Actinide and Transactinide Elements*; Springer, New York, **2006**; Vol. 2.
- [31] Morss, L. R.; Edelstein, N. M.; Fuger, J. *The Chemistry of Actinide and Transactinide Elements*; Springer, New York, **2006**; Vol. 3.
- [32] Kerridge, A. Quantification of F-Element Covalency through Analysis of the Electron Density: Insights from Simulation. *Chem. Commun.* **2017**, 53, 6685–6695. DOI: [10.1039/C7CC00962C](https://doi.org/10.1039/C7CC00962C).
- [33] Neidig, M. L.; Clark, D. L.; Martin, R. L. Covalency in F-Element Complexes. *Coord. Chem. Rev.* **2013**, 257(2), 394–406. DOI: [10.1016/j.ccr.2012.04.029](https://doi.org/10.1016/j.ccr.2012.04.029).
- [34] Pearson, R. G. Hard and Soft Acids and Bases. *J. Am. Chem. Soc.* **1963**, 85(22), 3533–3539. DOI: [10.1021/ja00905a001](https://doi.org/10.1021/ja00905a001).
- [35] Pearson, R. G. Hard and Soft Acids and Bases-the Evolution of a Chemical Concept. *Coord. Chem. Rev.* **1990**, 100(C), 403–425. DOI: [10.1016/0010-8545\(90\)85016-L](https://doi.org/10.1016/0010-8545(90)85016-L).
- [36] Pearson, R. G. Absolute Electronegativity and Hardness Correlated with Molecular Orbital Theory. *Proc. Natl. Acad. Sci. U. S. A.* **1986**, 83(November), 8440–8441. DOI: [10.1073/pnas.83.22.8440](https://doi.org/10.1073/pnas.83.22.8440).
- [37] Mincher, B. J.; Martin, L. R.; Schmitt, N. C.; Mincher, B. J.; Martin, L. R.; Schmitt, N. C.; Mincher, B. J.; Martin, L. R.; Schmitt, N. C. Diamylmethylphosphonate Solvent Extraction of Am (VI) from Nuclear Fuel Raffinate Simulant Solution. *Solvent Extr. Ion Exch.* **2012**, 30(5), 445–456. DOI: [10.1080/07366299.2012.671108](https://doi.org/10.1080/07366299.2012.671108).
- [38] Mincher, B. J.; Schmitt, N. C.; Tillotson, R. D.; Elias, G.; White, B. M.; Law, J. D.; Mincher, B. J.; Schmitt, N. C.; Tillotson, R. D.; Elias, G.; et al. Characterizing Diamylmethylphosphonate (DAAP) as an Americium Ligand for Nuclear Fuel-Cycle Applications. *Solvent Extr. Ion Exch.* **2014**, 32(2), 153–166.
- [39] Donnet, L.; Adnet, J. M.; Faure, N.; Bros, P.; Brossard, P.; Josso, F. Development of the SESAME Process. In *Proceedings of the 5th OECD-NEA International Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation-Session II (Partitioning)*; Mol, Belgium, **1998**; pp 25–27.
- [40] Law, J. D.; Mincher, B. J.; Tillotson, R. D.; Schmitt, N. C.; Grimes, T. S.; Law, J. D. Oxidation and Extraction of Am (VI) Using a Monoamidic Extractant in 3D Printed Centrifugal Contactors Particular Challenge Is the Development of a Partitioning. *J. Radioanal. Nucl. Chem.* **2018**, 318(1), 35–41. DOI: [10.1007/s10967-018-6126-4](https://doi.org/10.1007/s10967-018-6126-4).
- [41] Alyapyshev, M. Y.; Babain, V. A.; Tkachenko, L. I. Amides of Heterocyclic Carboxylic Acids as Novel Extractants for High-Level Waste Treatment. *Radiochemistry.* **2014**, 56 (6), 565–574. DOI: [10.1134/S1066362214060010](https://doi.org/10.1134/S1066362214060010).
- [42] Veliscek-Carolan, J. Separation of Actinides from Spent Nuclear Fuel: A Review. *J. Hazard. Mater.* **2016**, 318, 266–281. DOI: [10.1016/j.jhazmat.2016.07.027](https://doi.org/10.1016/j.jhazmat.2016.07.027).
- [43] Leoncini, A.; Huskens, J.; Verboom, W. Ligands for F-Element Extraction Used in the Nuclear Fuel Cycle. *Chem. Soc. Rev.* **2017**, 46, 7229–7273.
- [44] Ansari, S. A.; Pathak, P.; Mohapatra, P. K.; Vijay, K. Aqueous Partitioning of Minor Actinides by Different Processes. *Sep. Purif. Rev.* **2011**, 40, 43–76. DOI: [10.1080/15422119.2010.545466](https://doi.org/10.1080/15422119.2010.545466).

- [45] Bhattacharyya, A.; Mohapatra, P. K. Separation of Trivalent Actinides and Lanthanides Using Various 'N', 'S' and Mixed 'N, O' Donor Ligands: A Review. *Radiochim. Acta*. **2019**, *107*(9–11), 931–949.
- [46] Geist, A.; Adnet, J.; Bourg, S.; Ekberg, C.; Galán, H.; Guilbaud, P. An Overview of Solvent Extraction Processes Developed in Europe for Advanced Nuclear Fuel Recycling, Part 1 — Heterogeneous Recycling. *Sep. Sci. Technol.* **2020**, 1–16. DOI: [10.1080/01496395.2020.1795680](https://doi.org/10.1080/01496395.2020.1795680).
- [47] Ansari, S. A.; Pathak, P.; Mohapatra, P. K.; Manchanda, V. K. Chemistry of Diglycolamides: Promising Extractants for Actinide Partitioning. *Chem. Rev.* **2012**, *112*, 1751–1772.
- [48] Panak, P. J.; Geist, A. Complexation and Extraction of Trivalent Actinides and Lanthanides by Triazinylpyridine N - Donor Ligands. *Chem. Rev.* **2013**, *113*, 1199–1236. DOI: [10.1021/cr3003399](https://doi.org/10.1021/cr3003399).
- [49] Whittaker, D.; Geist, A.; Modolo, G.; Taylor, R.; Sarsfield, M.; Wilden, A. Applications of Diglycolamide Based Solvent Extraction Processes in Spent Nuclear Fuel Reprocessing, Part 1: TODGA. *Solvent Extr. Ion Exch.* **2018**, *36*(3), 223–256. DOI: [10.1080/07366299.2018.1464269](https://doi.org/10.1080/07366299.2018.1464269).
- [50] Ruhela, R.; Singh, A. K.; Tomar, B. S.; Hubli, R. C. RSC Advances Separation of Palladium from High Level Liquid Waste – A Review. *RSC Advances*. **2014**, *4*, 24344–24350.
- [51] Thompson, M. C. Distribution of Selected Lanthanides and Actinides between 30% TBP in N-Paraffin and Various Metal Nitrate Solutions. **1973**, 29. <https://www.osti.gov/biblio/4410678>
- [52] Watanabe, K.; Ono, R. The Extraction of Curium and Americium by Tri-n-Octyl Oxide Phosphine. *J. Nucl. Sci. Technol.* **1964**, *1*(2), 75–76. DOI: [10.1080/18811248.1964.9732082](https://doi.org/10.1080/18811248.1964.9732082).
- [53] Gharibyan, N.; Dailey, A.; Mclain, D. R.; Evelyn, M.; Moody, W. A.; Happel, S.; Sudowe, R. Solvent Extraction and Ion Exchange Extraction Behavior of Americium and Curium on Selected Extraction Chromatography Resins from Pure Acidic Matrices. *Solvent Extr. Ion Exch.* **2014**, *32*(4), 37–41. DOI: [10.1080/07366299.2014.884888](https://doi.org/10.1080/07366299.2014.884888).
- [54] Madic, C.; Testard, F.; Hudson, M. J.; Liljenzin, J.-O.; Christiansen, B.; FERRANDO, M.; Facchini, A.; Geist, A.; Modolo, G.; Gonzales-Espartero, A.; et al. *Partnew New Solvent Extraction Processe for Minor Actinides Final Report*; Marcoule, **2004**. <https://www.osti.gov/etdeweb/biblio/20583423>
- [55] Marie, C.; Kaufholz, P.; Vanel, V.; Duchesne, M. T.; Russello, E.; Faroldi, F.; Baldini, L.; Casnati, A.; Wilden, A.; Modolo, G.; et al. Development of a Selective Americium Separation Process Using H4TPAEN as Water-Soluble Stripping Agent. *Solvent Extr. Ion Exch.* **2019**, *37*(5), 313–327.
- [56] Matveev, P. I.; Petrov, V. G.; Egorova, B. V.; Senik, N. N.; Semenkov, A. S.; Dubovaya, O. V.; Valkov, A. V.; Kalmykov, S. N. Solvent Extraction of Rare Earth Elements by Tri-n-Butyl Phosphate and Tri-Iso-Amyl Phosphate in the Presence of Ca(NO₃)₂. *Hydrometallurgy*. **2018**, *175*(July 2017), 218–223. DOI: [10.1016/j.hydromet.2017.12.007](https://doi.org/10.1016/j.hydromet.2017.12.007).
- [57] Lu, D.; Horng, J. S.; Hoh, Y. C. The Separation of Neodymium by Quaternary Amine from Didymium Nitrate Solution. *J. Less-Common Met.* **1989**, *149*(C), 219–224. DOI: [10.1016/0022-5088\(89\)90489-X](https://doi.org/10.1016/0022-5088(89)90489-X).
- [58] Xie, F.; Zhang, T. A.; Dreisinger, D.; Doyle, F.; Critical, A. Review on Solvent Extraction of Rare Earths from Aqueous Solutions. *Miner. Eng.* **2014**, *56*, 10–28. DOI: [10.1016/j.mineng.2013.10.021](https://doi.org/10.1016/j.mineng.2013.10.021).
- [59] Firm, T. H. E.; Karlf, O. F. Patent Application Publication (10) Pub. No.: US 2007/0009410 A1, **2007**.
- [60] Modolo, G.; Nabet, S. Thermodynamic Study on the Synergistic Mixture of Bis(Chlorophenyl) Dithiophosphinic Acid and Tris (2- Ethylhexyl) Phosphate for

- Separation of Actinides (III) from Lanthanides (III). *Solvent Extr. Ion Exch.* **2005**, 23 (November 2015), 359–373. DOI: [10.1081/SEI-200056515](https://doi.org/10.1081/SEI-200056515).
- [61] Modolo, G.; Odoj, R. Synergistic Selective Extraction of Actinides (III) over Lanthanides from Nitric Acid Using New Aromatic Diorganyldithiophosphinic Acids and Neutral Organophosphorus Compounds. *Solvent Extr. Ion Exch.* **1999**, 17(1), 33–53. DOI: [10.1080/07360299908934599](https://doi.org/10.1080/07360299908934599).
- [62] Suzuki, H.; Tsubata, Y.; Kurosawa, T.; Sagawa, H.; Matsumura, T. Continuous Extraction and Separation of Am(III) and Cm(III) Using a Highly Practical Diamide Amine Extractant. *J. Nucl. Sci. Technol.* **2017**, 54(11), 1163–1167. DOI: [10.1080/00223131.2017.1299050](https://doi.org/10.1080/00223131.2017.1299050).
- [63] Madic, C.; Hudson, M. *High-level Liquid Waste Partitioning by Means of Completely Incinerable Extractants*; EUR 18038; European Commission: Luxembourg, 1998.
- [64] Suzuki, H.; Tsubata, Y.; Urosawa, T. K.; Shibata, M.; Kawasaki, T.; Urabe, S.; Matsumura, T. Highly Practical and Simple Ligand for Separation of Am (III) and Eu (III) from Highly Acidic Media. *Anal. Sci.* **2016**, 32(April), 477–479. DOI: [10.2116/analsci.32.477](https://doi.org/10.2116/analsci.32.477).
- [65] Suzuki, H.; Tsubata, Y.; Matsumura, T. High-Performance Alkyl Diamide Amine and Water-Soluble Diamide Ligand for Separating of Am (III) from Cm (III). *Anal. Sci.* **2017**, 33, 239–242. DOI: [10.2116/analsci.33.239](https://doi.org/10.2116/analsci.33.239).
- [66] Stephan, H.; Gloe, K.; Beger, J.; Mühl, P. Liquid-Liquid Extraction of Metal Ions with Amido Podands. *Solvent Extr. Ion Exch.* **1991**, 9(3), 459–469. DOI: [10.1080/07366299108918064](https://doi.org/10.1080/07366299108918064).
- [67] Kaneko, M.; Suzuki, H.; Matsumura, T. Theoretical Elucidation of Am(III)/Cm(III) Separation Mechanism with Diamide-Type Ligands Using Relativistic Density Functional Theory Calculation. *Inorg. Chem.* **2018**, 57(23), 14513–14523. DOI: [10.1021/acs.inorgchem.8b01624](https://doi.org/10.1021/acs.inorgchem.8b01624).
- [68] Alyapyshev, M.; Babain, V.; Tkachenko, L.; Kenf, E.; Voronaev, I.; Dar'in, D.; Matveev, P.; Petrov, V.; Kalmykov, S.; Ustynyuk, Y. Extraction of Actinides with Heterocyclic Dicarboxamides. *J. Radioanal. Nucl. Chem.* **2018**, 316(2), 419–428. DOI: [10.1007/s10967-018-5775-7](https://doi.org/10.1007/s10967-018-5775-7).
- [69] Kirsanov, D. O.; Borisova, N. E.; Reshetova, M. D.; Ivanov, A. V.; Korotkov, L. A.; Eliseev, I. I.; Alyapyshev, M. Yu.; Spiridonov I. G.; Legin, A. V.; Vlasov Yu. G.; Babain, V. A. Novel Diamides of 2, 2' Dipyridyl 6, 6' Dicarboxylic Acid : Synthesis, Coordination Properties, and Possibilities of Use in Electrochemical Sensors and Liquid Extraction. *Russ. Chem. Bull.* **2012**, 61(4), 881–890. DOI: [10.1007/s11172-012-0124-4](https://doi.org/10.1007/s11172-012-0124-4).
- [70] Alyapyshev, M. Y.; Babain, V. A.; Tkachenko, L. I.; Eliseev, I. I.; Didenko, A. V.; Petrov, M. L. Dependence of Extraction Properties of 2,6-Dicarboxypyridine Diamides on Extractant Structure. *Solvent Extr. Ion Exch.* **2011**, 29(4), 619–636. DOI: [10.1080/07366299.2011.581049](https://doi.org/10.1080/07366299.2011.581049).
- [71] Matveev, P. I.; Mitrofanov, A. A.; Petrov, V. G.; Zhokhov, S. S.; Smirnova, A. A.; Ustynyuk, Y. A.; Kalmykov, S. N. Testing A Simple Approach for Theoretical Evaluation of Radiolysis Products in Extraction Systems. A Case of N,O-Donor Ligands for Am/Eu Separation. *RSC Adv.* **2017**. DOI: [10.1039/C7RA11622E](https://doi.org/10.1039/C7RA11622E).
- [72] Matveev, P. I.; Borisova, N. E.; Andreadi, N. G.; Zakirova, G. G.; Petrov, V. G.; Belova, E. V.; Kalmykov, S. N.; Myasoedov, B. F. A First Phosphine Oxide-Based Extractant with High Am/Cm Selectivity. *Dalt. Trans.* **2019**, 48, 2554–2559. DOI: [10.1039/C8DT04729D](https://doi.org/10.1039/C8DT04729D).
- [73] Hudson, M. J.; Lewis, F. W.; Harwood, L. M. *The Circuitous Journey from Malonamides to BTPPhens: Ligands for Separating Actinides from Lanthanides*, 1st ed. ed.; Elsevier Ltd., Amsterdam, **2013**; Vol. 9.

- [74] Hudson, M. J.; Harwood, L. M.; Laventine, D. M.; Lewis, F. W. Use of Soft Heterocyclic N - Donor Ligands to Separate Actinides and Lanthanides. *Inorg. Chem.* **2013**, 52(7), 3414–3428. DOI: [10.1021/ic3008848](https://doi.org/10.1021/ic3008848).
- [75] Afsar, A.; Harwood, L. M.; Hudson, M. J.; Westwood, J.; Geist, A. Effective Separation of the Actinides Am(III) and Cm(III) by Electronic Modulation of Bis-(1,2,4-Triazin-3-Yl) Phenanthrolines. *Chem. Commun.* **2015**, 51(27), 5860–5863. DOI: [10.1039/C5CC00567A](https://doi.org/10.1039/C5CC00567A).
- [76] Ashfaq Afsar, A. C.; Edwards, A. G.; Harwood, L. M.; Hudson, M. J.; James Westwood, R. C. W. Effective Separation of Am(III) from Cm(III) Using Modified BTPhen Ligands. *Heterocycles*. **2017**, 95(1), 575–586. DOI: [10.3987/COM-16-S\(S\)26](https://doi.org/10.3987/COM-16-S(S)26).
- [77] Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G. B.; Desreux, J. F.; Bouslimani, N.; Modolo, G.; Wilden, A.; Sypula, M.; Vu, T.; et al. Highly Efficient Separation of Actinides from Lanthanides by a Phenanthroline-Derived Bis-Triazine Ligand. *J. Am. Chem. Soc.* **2011**, 13093–13102. DOI: [10.1021/ja203378m](https://doi.org/10.1021/ja203378m).
- [78] Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Afsar, A.; Laventine, D. M.; Štastná, K.; John, J.; Distler, P. Separation of the Minor Actinides Americium(III) and Curium(III) by Hydrophobic and Hydrophilic BTPhen Ligands: Exploiting Differences in Their Rates of Extraction and Effective Separations at Equilibrium. *Solvent Extr. Ion Exch.* **2018**, 36(2), 115–135. DOI: [10.1080/07366299.2018.1429358](https://doi.org/10.1080/07366299.2018.1429358).
- [79] Distler, P.; Stamberg, K.; John, J.; Harwood, L. M.; Frank, W.; Distler, P.; Stamberg, K.; John, J.; Harwood, L. M.; Frank, W. Modelling of the Am (III) – Cm (III) Kinetic Separation Effect Observed during Metal Ion Extraction by Bis-(1,2,4)-Triazine Ligands. *Sep. Sci. Technol.* **2018**, 53(2), 277–285. DOI: [10.1080/01496395.2017.1384017](https://doi.org/10.1080/01496395.2017.1384017).
- [80] Nash, K. L. The Chemistry of TALSPEAK: A Review of the Science. *Solvent Extr. Ion Exch.* **2015**, 33(1), 37–41. DOI: [10.1080/07366299.2014.985912](https://doi.org/10.1080/07366299.2014.985912).
- [81] Sasaki, Y.; Tsubata, Y.; Kitatsuji, Y.; Sugo, Y.; Shirasu, N.; Novel Extractant, M. Y. NTAamide, and Its Combination with TEDGA for Mutual Separation of Am/Cm/Ln. *Solvent Extr. Ion Exch.* **2014**, 32(2), 179–188. DOI: [10.1080/07366299.2013.836422](https://doi.org/10.1080/07366299.2013.836422).
- [82] Sasaki, Y.; Tsubata, Y.; Kitatsuji, Y.; Sugo, Y.; Shirasu, N.; Morita, Y.; Kimura, T. Extraction Behavior of Metal Ions by TODGA, DOODA, MIDOA, and NTAamide Extractants from HNO₃ to n-Dodecane. *Solvent Extr. Ion Exch.* **2013**, 31(4), 401–415. DOI: [10.1080/07366299.2013.800431](https://doi.org/10.1080/07366299.2013.800431).
- [83] Chapron, S.; Marie, C.; Arrachart, G.; Miguiditchian, M.; New, P.-R. S. Insight into the Americium/Curium Separation by Solvent Extraction Using Diglycolamides. *Solvent Extr. Ion Exch.* **2015**, 33(3), 236–248. DOI: [10.1080/07366299.2014.1000792](https://doi.org/10.1080/07366299.2014.1000792).
- [84] Charbonnel, M.; Berthon, C.; Berthon, L.; Boubals, N.; Burdet, F.; Duchesne, M.; Mabilille, N.; Petit, S.; Zorz, N. Complexation of Ln (III) and Am (III) with the Hydrosoluble TEDGA : Speciation and Thermodynamics Studies. *Procedia Chem.* **2012**, 7, 20–26. DOI: [10.1016/j.proche.2012.10.005](https://doi.org/10.1016/j.proche.2012.10.005).
- [85] Charpon, S.; Maria, C.; Pacary, V.; Duchesne, M. T.; Arrachart, G.; Pellet-Rostaing, S.; Miguiditchian, M. Separation of Americium by Liquid-Liquid Extraction Using Diglycolamides Water-Soluble Complexing Agents. *Procedia Chem.* **2016**, 21, 133–139. DOI: [10.1016/j.proche.2016.10.019](https://doi.org/10.1016/j.proche.2016.10.019).
- [86] Klaß, L.; Wilden, A.; Kreft, F.; Wagner, C.; Geist, A.; Panak, P. J.; Herdzyk-Koniecko, I.; Narbutt, J.; Modolo, G. Evaluation of the Hydrophilic Complexant N,N,N',N'-Tetraethyldiglycolamide (TEDGA) and Its Methyl-Substituted Analogues in the Selective Am(III) Separation. *Solvent Extr. Ion Exch.* **2019**, 37(5), 297–312. DOI: [10.1080/07366299.2019.1651039](https://doi.org/10.1080/07366299.2019.1651039).
- [87] Gujar, R. B.; Ansari, S. A.; Mohapatra, P. K.; Leoncini, A.; Werboom, W. Solid Phase Extraction of Am (III) and Cm (III) from Acidic Feeds Using Tetraethyl Diglycolamide (TEDGA) in Ionic Liquid. *J. Radioanal. Nucl. Chem.* **2016**, 309(2), 819–825.

- [88] Lange, S.; Wilden, A.; Modolo, G.; Sadowski, F.; Bosbach, D.; Lange, S.; Wilden, A.; Modolo, G.; Sadowski, F.; Lange, S.; et al. Direct Selective Extraction of Trivalent Americium from PUREX Raffinate Using A Combination of CyMe4BTPhen and TEDGA — A Feasibility Study. *Solvent Extr. Ion Exch.* **2017**, *35*(3), 161–173.
- [89] Zsabka, P.; Van, H. K.; Wilden, A.; Modolo, G.; Verwerft, M.; Binnemans, K.; Cardinaels, T. Selective Extraction of Americium from Curium and the Lanthanides by the Lipophilic Ligand CyMe4BTPhen Dissolved in Aliquat-336 Nitrate Ionic Liquid. *Solvent Extr. Ion Exch.* **2020**, *38*(2), 194–211. DOI: [10.1080/07366299.2019.1708006](https://doi.org/10.1080/07366299.2019.1708006).
- [90] Wilden, A.; Modolo, G.; Kaufholz, P.; Sadowski, F.; Lange, S.; Sypula, M.; Magnusson, D.; Müllich, U.; Geist, A.; Bosbach, D. Laboratory-Scale Counter-Current Centrifugal Contactor Demonstration of an Innovative-SANEX Process Using a Water Soluble BTP. *Solvent Extr. Ion Exch.* **2015**, *33*(2), 91–108. DOI: [10.1080/07366299.2014.952532](https://doi.org/10.1080/07366299.2014.952532).
- [91] Geist, A.; Müllich, U.; Magnusson, D.; Kaden, P.; Modolo, G.; Wilden, A.; Zevaco, T. Actinide(III)/Lanthanide(III) Separation via Selective Aqueous Complexation of Actinides(III) Using a Hydrophilic 2,6-Bis(1,2,4-Triazin-3-Yl)-Pyridine in Nitric Acid. *Solvent Extr. Ion Exch.* **2012**, *30*(5), 433–444. DOI: [10.1080/07366299.2012.671111](https://doi.org/10.1080/07366299.2012.671111).
- [92] Wagner, C.; Müllich, U.; Geist, A.; Panak, P. J. Selective Extraction of Am(III) from PUREX Raffinate: The AmSel System. *Solvent Extr. Ion Exch.* **2016**, *34*(2), 103–113. DOI: [10.1080/07366299.2015.1129192](https://doi.org/10.1080/07366299.2015.1129192).
- [93] Kaufholz, P.; Modolo, G.; Wilden, A.; Sadowski, F.; Bosbach, D.; Wagner, C.; Geist, A.; Panak, P. J.; Lewis, F. W.; Harwood, L. M. Solvent Extraction and Fluorescence Spectroscopic Investigation of the Selective Am(III) Complexation with TS-BTPhen. *Solvent Extr. Ion Exch.* **2016**, *34*(2), 126–140. DOI: [10.1080/07366299.2016.1151308](https://doi.org/10.1080/07366299.2016.1151308).
- [94] Schimmelpfennig, B.; Narbutt, J.; Geist, A.; Panak, P. J. Do An(III) and Ln(III) Ions Form Heteroleptic Complexes with Diglycolamide and Hydrophilic BT(B)P Ligands in Solvent Extraction Systems? A Spectroscopic and DFT Study. *New J. Chem.* **2019**, *43*, 6314–6322. DOI: [10.1039/C9NJ00651F](https://doi.org/10.1039/C9NJ00651F).
- [95] Kaufholz, P.; Sadowski, F.; Wilden, A.; Modolo, G.; Lewis, F. W.; Smith, A. W.; Harwood, L. M. TS-BTPhen as a Promising Hydrophilic Complexing Agent for Selective Am (III) Separation by Solvent Extraction. *Nukleonika*. **2015**, *60*(August), 815–820. DOI: [10.1515/nuka-2015-0120](https://doi.org/10.1515/nuka-2015-0120).
- [96] Modolo, G.; Wilden, A.; Kaufholz, P.; Bosbach, D.; Geist, A. Development and Demonstration of Innovative Partitioning Processes (I-sanex and 1-Cycle SANEX) for Actinide Partitioning. *Prog. Nucl. Energy*. **2014**, *72*, 107–114. DOI: [10.1016/j.pnucene.2013.07.021](https://doi.org/10.1016/j.pnucene.2013.07.021).
- [97] Malmbeck, R.; Magnusson, D.; Bourg, S.; Carrott, M.; Geist, A.; Hérès, X.; Miguirditchian, M.; Modolo, G.; Müllich, U.; Sorel, C.; et al. Homogenous Recycling of Transuranium Elements from Irradiated Fast Reactor Fuel by the EURO- GANEX Solvent Extraction Process. *Radiochim. Acta*. **2019**, *107*(9–11), 917–929.
- [98] Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Geist, A.; Kozhevnikov, V. N.; John, J. Hydrophilic Sulfonated Bis-1,2,4-Triazine Ligands are Highly Effective Reagents for Separating Actinides(III) from Lanthanides(III) via Selective Formation of Aqueous Actinide Complexes. *Chem. Sci.* **2015**, *6*, 4812–4821. DOI: [10.1039/C5SC01328C](https://doi.org/10.1039/C5SC01328C).
- [99] Jensen, M. P.; Chiarizia, R.; Shkrob, I. A.; Ulicki, J. S.; Spindler, B. D.; Murphy, D. J.; Hossain, M.; Roca-Sabio, A.; Platas-Iglesias, C.; De Blas, A.; et al. Aqueous Complexes for Efficient Size-Based Separation of Americium from Curium. *Inorg. Chem.* **2014**, *53* (12), 6003–6012.
- [100] Jensen, M. P.; Chiarizia, R.; Ulicki, J. S.; Spindler, B. D.; Murphy, D. J.; Hossain, M. M.; Roca-Sabio, A.; de Blas, A.; Rodríguez-Blas, T. Solvent Extraction Separation of Trivalent

- Americium from Curium and the Lanthanides. *Solvent Extr. Ion Exch.* **2015**, 33(4), 329–345. DOI: [10.1080/07366299.2015.1046292](https://doi.org/10.1080/07366299.2015.1046292).
- [101] Borrini, J.; Lemaire, M.; Gracia, S.; Arrachart, G.; Bernier, G.; Hérès, X.; Hill, C.; Lemaire, M.; Gracia, S.; Arrachart, G.; et al. Water Soluble PDCA Derivatives for Selective Ln (III)/an (III) and Am (III)/cm (III) Separation. *Solvent Extr. Ion Exch.* **2015**, 33(3), 224–235.
- [102] Vanel, V.; Marie, C.; Kaufholz, P.; Montuir, M.; Boubals, N.; Wilden, A.; Modolo, G.; Geist, A.; Sorel, C. Modeling and Flowsheet Design of an Am Separation Process Using TODGA and H4TPAEN. *Procedia Chem.* **2016**, 21, 223–230. DOI: [10.1016/j.proche.2016.10.032](https://doi.org/10.1016/j.proche.2016.10.032).
- [103] Gracia, S.; Arrachart, G.; Marie, C.; Chapron, S.; Miguiditchian, M.; Pellet-Rostaing, S. Separation of Am (III) by Solvent Extraction Using Water-Soluble H4tpaen Derivatives. *Tetrahedron.* **2015**, 71(33), 5321–5336. DOI: [10.1016/j.tet.2015.06.015](https://doi.org/10.1016/j.tet.2015.06.015).
- [104] Boubals, N.; Wagner, C.; Dumas, T.; Manie, G.; Kaufholz, P.; Panak, P. J.; Modolo, G.; Geist, A.; Guilbaud, P. Complexation of Actinide(III) and Lanthanide(III) with H4TPAEN for a Separation of Americium from Curium and Lanthanides. *Inorg. Chem.* **2017**, 56, 7861–7869. DOI: [10.1021/acs.inorgchem.7b00603](https://doi.org/10.1021/acs.inorgchem.7b00603).
- [105] Huang, P.-W.; Wang, C.-Z.; Wu, Q.-Y.; Lan, J.-H.; Song, G.; Chai, Z.-F.; Shi, W.-Q. Understanding Am³⁺/Cm³⁺ Separation with H4TPAEN and Its Hydrophilic Derivatives: A Quantum Chemical Study. *Phys. Chem. Chem. Phys.* **2018**, 20(20), 14031–14039.
- [106] Jensen, M. P.; Morss, L. R.; V; Ensor, B. J.; Aqueous, D. D. Complexation of Trivalent Lanthanide and Actinide Cations by N, N, N', N' -tetrakis(2-pyridylmethyl)ethylene-diamine. *J. Alloys Compd.* **2000**, 304, 137–141. DOI: [10.1016/S0925-8388\(00\)00620-4](https://doi.org/10.1016/S0925-8388(00)00620-4).
- [107] Sasaki, Y.; Kitatsuji, Y. Separation of Am, Cm and Lanthanides by Solvent Extraction with Hydrophilic and Lipophilic Organic Ligands. *Solvent Extr. Res. Dev. Jpn.* **2011**, 18, 93–101. DOI: [10.15261/serdj.18.93](https://doi.org/10.15261/serdj.18.93).
- [108] Ricano, A.; Abergel, R. J. Ultra-Selective Ligand-Driven Separation of Strategic Actinides. *Nat. Commun.* **2019**, 10(2438), 1–9.
- [109] Deblonde, G. J.; Abergel, R. J.; Lohrey, T. D.; An, D. D. Toxic Heavy Metal – Pb, Cd, Sn – Complexation by the Octadentate Hydroxypyridinonate Ligand Archetype 3,4,3-LI (1,2-HOPO). *New J. Chem.* **2018**, 42, 7649–7658. DOI: [10.1039/C7NJ04559J](https://doi.org/10.1039/C7NJ04559J).
- [110] Sturzbecher-Hoehne, B. M.; Deblonde, G. J.; Abergel, R. J. Solution Thermodynamic Evaluation of Hydroxypyridinonate UO₂(VI) and Th (IV) Decorporation. *Radiochim. Acta.* **2013**, 366, 359–366. DOI: [10.1524/ract.2013.2047](https://doi.org/10.1524/ract.2013.2047).
- [111] Modolo, G.; Kluxen, P.; Geist, A. Demonstration of the LUCA Process for the Separation of Americium(III) from Curium(III), Californium(III), and Lanthanides(III) in Acidic Solution Using a Synergistic Mixture of Bis(Chlorophenyl)Dithiophosphinic Acid and Tris(2--Ethylhexyl)Phosphate. *Radiochim. Acta.* **2010**, 98(4), 193–201. DOI: [10.1524/ract.2010.1708](https://doi.org/10.1524/ract.2010.1708).
- [112] Mishra, R. K.; Sudarsan, K. V.; Sengupta, P.; Vatsa, R. K.; Tyagi, A. K.; Kaushik, C. P.; Das, D.; Raj, K. Role of Sulfate in Structural Modifications of Sodium Barium Borosilicate Glasses Developed for Nuclear Waste Immobilization. *J. Am. Ceram. Soc.* **2008**, 91(12), 3903–3907. DOI: [10.1111/j.1551-2916.2008.02773.x](https://doi.org/10.1111/j.1551-2916.2008.02773.x).
- [113] Rostaing, C.; Poinssot, C.; Warin, D.; Baron, P.; Development, L. B. Validation of the EXAm Separation Process for Single Am Recycling. *Procedia Chem.* **2012**, 7, 367–373. DOI: [10.1016/j.proche.2012.10.057](https://doi.org/10.1016/j.proche.2012.10.057).
- [114] Vanel, V.; Bollesteros, M.-J.; Marie, C.; Montuir, M.; Pacary, V.; Antégnard, F.; Costenoble, S.; Boyer-Deslys, V. Consolidation of the EXAm Process: Towards the Reprocessing of a Concentrated PUREX Raffinate. *Procedia Chem.* **2016**, 21, 190–197. DOI: [10.1016/j.proche.2016.10.027](https://doi.org/10.1016/j.proche.2016.10.027).

- [115] Li, X.; Zhou, L.; Yan, L.; Dong, Y.; Bai, Z.; Sun, X.; Diwu, J.; Wang, S.; Bünzli, J.; Sun, Q. A Supramolecular Lanthanide Separation Approach Based on Multivalent Cooperative Enhancement of Metal Ion Selectivity. *Nat. Commun.* **2018**, 9(547), 1–10.
- [116] Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G. B.; Wilden, A.; Sypula, M.; Modolo, G.; Vu, T.; Vidick, G.; Bouslimani, N.; et al. From BTBPs to BTPhens : The Effect of Ligand Pre-Organization on the Extraction Properties of Quadridentate Bis-Triazine Ligands. *Procedia Chem.* **2012**, 7, 231–238. DOI: [10.1016/j.proche.2012.10.038](https://doi.org/10.1016/j.proche.2012.10.038).
- [117] Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G. B. BTBPs versus BTPhens: Some Reasons for Their Differences in Properties Concerning the Partitioning of Minor Actinides and the Advantages of BTPhens. *Inorg. Chem.* **2013**, 52(9), 4993–5005. DOI: [10.1021/ic3026842](https://doi.org/10.1021/ic3026842).