

Reference composition of the fission product and rest waste stream

ASOF WP3

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Glossary of abbreviations

An	Actinides
ASOF	Advanced Separation for Optimal management of spent Fuel
CyMe4-BTBP	6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzol[1,2,4]triazin-3-yl)[2,2]bipyridine
DIAMEX	DIAMide EXtraction
DMDOHEMA	<i>N,N'</i> -dimethyl, <i>N,N'</i> -dioctylhexylethoxymalonamide
ETF	Energietransitiefonds
FAP	Fission and Activation Products
FP	Fission Products
HAR	Highly Active Raffinate
HEDTA	<i>N</i> -(2-Hydroxyethyl)ethylenediaminetriacetic acid
HIP	Hot Isostatic Press
Ln	Lanthanides
PUREX	Plutonium Uranium Redox EXtraction
SANEX	Selective ActiNide EXtraction
TBP	Tributyl Phosphate
T _{HM}	Ton of Heavy Metal (= uranium metal)
TODGA	<i>N,N,N',N'</i> -tetraoctyl diglycolamide
TRL	Technology Readiness Level

Preface

This report was written for WP3 of the ETF 2018 research project ASOF – Advanced Separation for Optimal management of spent Fuel, supported by the Belgian authorities, contract number CO-90-18-4699-00. It was not foreseen as an official contractual deliverable, but it contains information that is essential for the preparation and testing of samples that will result in deliverables D3.1.1 (Proof of concept conditioning cesium/strontium), D3.1.2 (Durability and performance of conditioned Cs/Sr), D3.2.1 (Proof of concept conditioning rest fraction) and D3.2.2 (Durability and performance of conditioned rest fraction).

Abstract

This document was written in the framework of research project ASOF – Advanced Separation for Optimal management of spent Fuel, supported by the Belgian authorities. This project investigates the effects of potential partitioning and transmutation on the disposal of spent fuel. The considered advanced processing would result in two main waste streams: a heat generating Cs/Sr rich waste stream, and a rest waste stream that contains all the other waste components. In this report, reference compositions are presented for these two waste streams. These compositions can be used to prepare simulated waste forms whose leaching behaviour will be studied further in ASOF.

Keywords

ASOF, partitioning, transmutation, waste stream, immobilization, ceramic, geopolymers

1. Introduction

This document is written in the frame of research project ASOF – Advanced Separation for Optimal management of spent Fuel, supported by the Belgian authorities. This project investigates the effects of potential partitioning and transmutation on the disposal of spent fuel.

In the ASOF approach, the higher actinides and short lived fission products will be separated from the U, Pu and Np. In subsequent extractions, the Am(III) would be concentrated in a solution that can be used to produce transmutation targets. The process scheme thereby generates several raffinate solutions as side products containing fission products and minor actinides. By separation of the heat emitting Cs and Sr and immobilization in a specific waste matrix, the lower heat emission of the rest fraction could allow using a smaller disposal surface for this rest fraction.

The ASOF project consists of four work packages.

- WP1. Separation of higher actinides and short lived fission products from irradiated fuel
- WP2. Conversion of the americium concentrate to oxide for the production of transmutation targets
- WP3. Conditioning of waste groups resulting from a partitioning scenario
- WP4. Impact of advanced separation on the geological disposal installation

This document is based on output from WP1 and will be used in WP3, as explained further hereunder.

In WP1 separation methods are developed that will in principle result in (at least) two waste streams:

- A Cs/Sr rich solution

- A solution rich in other Fission and Activation Products (FAP) and smaller amounts of lanthanides ('Ln') and actinides ('An'). WP1 provides data on the possible composition of the raffinates from the considered advanced processing methods. These data are used in this report to define a reference waste stream composition for use in WP3. The possible compositions of the raffinates were based on published literature, mainly based on demonstrations in the framework of EU projects. For the methods developed in the framework of ASOF, the technology readiness level (TRL) is much lower. Hence, the effect of these methods on the waste stream composition was not taken into account.

The exact composition of the waste streams will depend on the separation methods. Because at the time this report was written, the separation method development was still ongoing, a composition that will exactly match the separation methods in development cannot be given. Instead, the reference waste stream composition will be defined based on a literature study performed in WP1 (report I-0963) [1]. The latter report contains data for the expected composition of the raffinates before separation of Cs and Sr. For the definition of the reference composition of the two considered waste streams, certain assumptions have to be made, as explained further in this document.

WP3 of ASOF investigates possible waste matrices that could be suitable for the waste streams defined in WP1. Samples will be prepared and their durability will be tested in simplified reference disposal conditions. Two types of matrices will be studied: alkali-activated materials and matrices resulting from thermal treatment. There is a particular interest in the investigation of the conditioning by HIP-ing (Hot Isostatic Pressing). One of the criteria will be also the possibility for the upscaling of the technology and treatment from inactive lab tests to highly-active real waste streams. This will not be tested, but it can be evaluated theoretically. All tests would be done with inactive materials.

In the next section (section 2) we give a summary of the advanced reprocessing scheme that is considered in the literature study report I-0963 [1]. In section 3, the data from [1] are interpreted to obtain a complete composition of the expected waste streams. In section 4, these complete compositions are simplified following given criteria to define reference compositions for the Cs/Sr waste stream and the rest waste stream. Section 5 gives the brief conclusions and perspectives.

2. Advanced reprocessing scheme

The subsequent separation processes that would lead to the separation of Am is shown in Figure 1, taken from report I-0963 [1]. The U, Pu, Np solution and the Am product solution are the end products. The other solutions are waste streams that have to be disposed of. There are thus four waste streams: (1) a Tc rich solution, (2) the DIAMEX raffinate (rich in FAP, with lower concentrations of An and Ln), (3) the SANEX raffinate (rich in Ln), and (4) a Cm enriched solution.

The Cs and Sr separation is not included in this advanced reprocessing scheme. The DIAMEX raffinate still includes the Cs and Sr. These will be extracted in a separate step, not yet described in report I-0963 [1]. This will modify the composition of the DIAMEX raffinate. We will thus have to deal not with the 'DIAMEX raffinate' but with a 'modified DIAMEX raffinate' (Figure 2). The Cs and Sr concentration will be much lower in the modified DIAMEX raffinate, but it is not clear if some fission products other than Cs and Sr will still be present in this modified DIAMEX raffinate, or will go to the Cs/Sr solution. In the assumption that most of the other fission products will remain in the modified DIAMEX raffinate, the composition of the modified DIAMEX raffinate would not be very different from the original DIAMEX raffinate, but will not contain the Cs and Sr and some elements that may be co-extracted. This (modified) DIAMEX raffinate can be described as a solution with a large number of different An, Ln and FAP, but the concentrations of the FP will be higher than the concentrations of An and Ln, so it is mainly a FAP waste stream.

The SANEX raffinate has high Ln concentrations, low Am and Cm concentrations, and some yttrium, but contains no FAP. So its composition is very different from the DIAMEX raffinate.

The Cs and Sr waste stream would have a Cs/Sr molar ratio of about 2¹. At the time this report was written, it was not yet clear what would be their concentration in an optimized separation scheme, which other radionuclides would be present, what the solvent would be, and what the amounts of organic or inorganic compounds would be. This work in WP1 of ASOF still had to be done. It is also possible that the Cs will be separated from the Sr in two different waste streams, but this is currently not the reference scenario.

¹ According to the Cs and Sr concentrations reported in mg/L in Table 9 of SCK CEN report I-0963 [1], converted to Mol·L⁻¹, the molar ratio would be 2.1. On a short time scale the cooling time has minimal effect on the ratio.

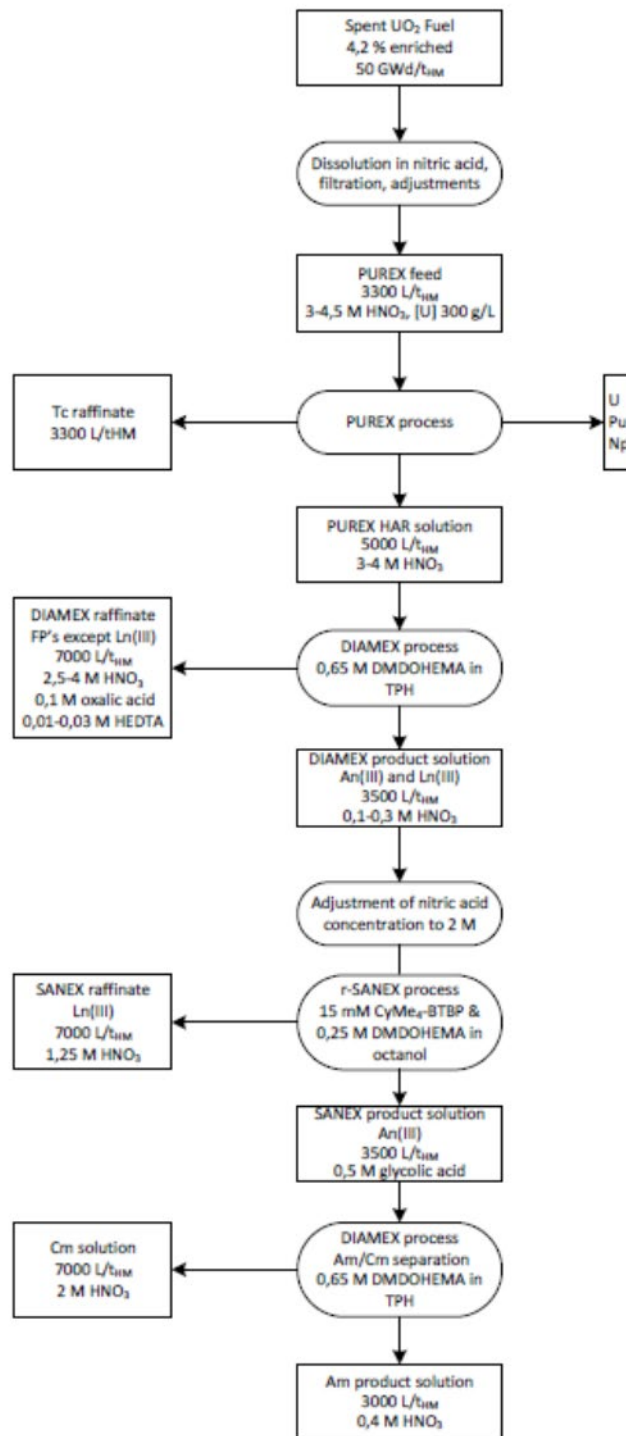


Figure 1: Advanced reprocessing scheme in report I-0963 [1].

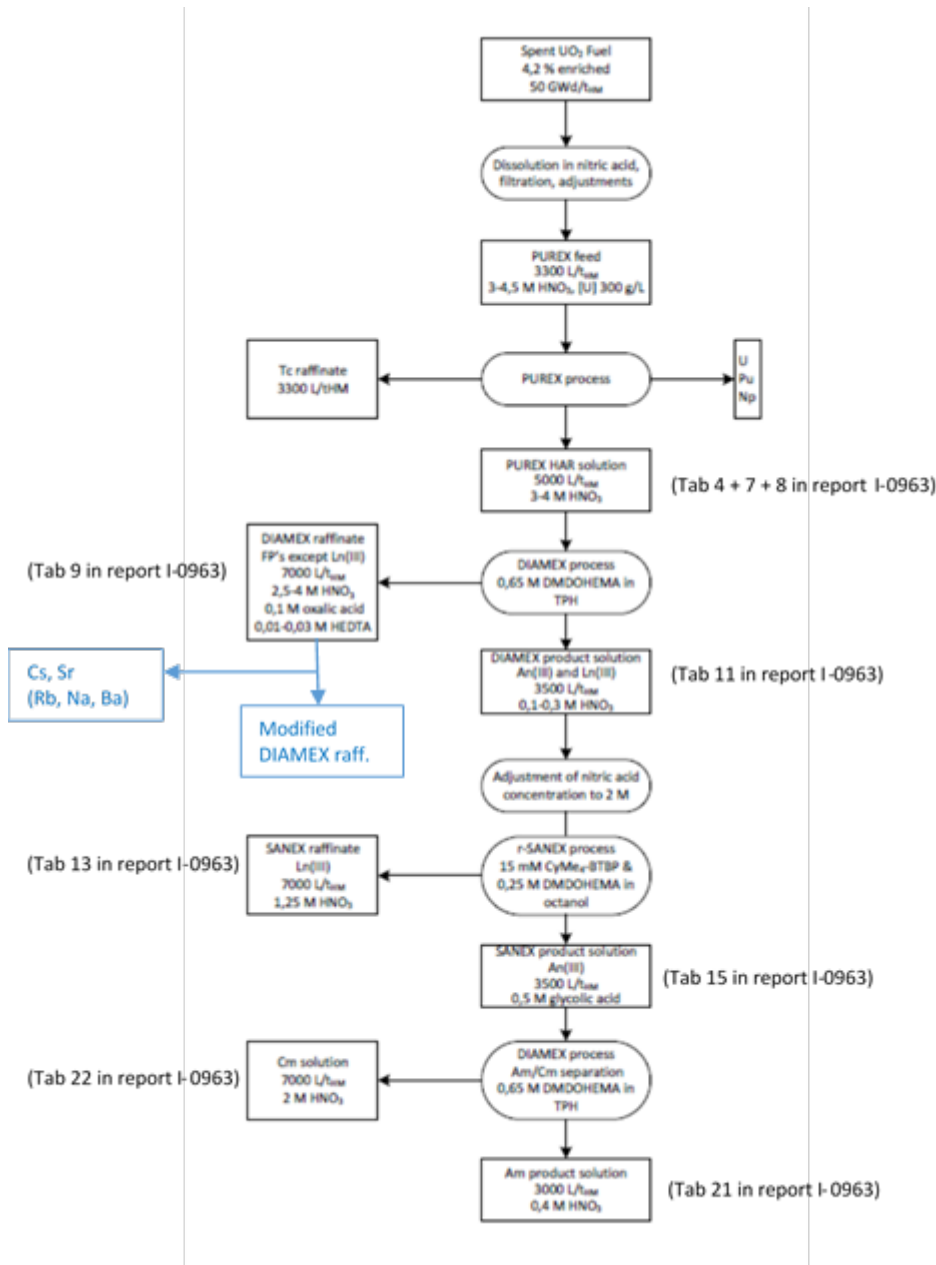


Figure 2: Modified advanced reprocessing scheme from report I-0963 [1], including Cs and Sr separation.

3. Composition of the waste streams

Based on the scheme presented in Figure 2 of section 2, three waste streams are considered: the (modified) DIAMEX raffinate, the SANEX raffinate, and the curium solution, respectively. The Tc raffinate is at this moment not considered, because we do not have a detailed composition, and because the addition of Tc to the test samples in WP3 is anyway not considered, as this element exists only as radioactive isotopes. The U/Pu/Np solution is further purified, resulting in a Np waste stream. Because we don't have data about the amount of Np in this waste stream, it is not considered further.

Hereunder (section 3.1, 3.2 and 3.3) we present the composition of the three separate waste streams, based on report I-0963 [1] and the composition of the mixed waste stream, assuming that the three waste streams would be poured together to have only one final solution that has to be conditioned. The latter composition is given in section 3.4. The radionuclide inventory in report I-0963 that is used here, was calculated for spent UO₂ fuel, 4.2% ²³⁵U enrichment, configuration 15x15, burnup 50 GWd/tHM after 10 years of cooling.

3.1 Composition of the (modified) DIAMEX raffinate

The proposed reference composition of the (modified) DIAMEX raffinate, i.e. the waste stream with the FP and smaller amounts of minor actinides and Ln, is given in Table 1 and Figure 3. It is based on the data from Table 9 in report I-0963 [1]. The data in the latter report were expressed in mg·L⁻¹. In Table 1 they are expressed on Mol·L⁻¹ and ordered from high to low concentration. Minor actinides are shown in red, lanthanides in green, and FAP in black. Sr and Cs (in blue) are included, but if they are extracted in a separate solution (waste stream) as shown in Figure 2, a modified DIAMEX raffinate is obtained with much lower Cs and Sr concentration. Ba and Rb (also in blue) would be co-extracted with Sr and Cs, and thus appear also in the Sr and Cs waste stream.

Table 1: Elemental concentrations expected in the DIAMEX raffinate, ordered from high to low concentration and assuming Cs, Sr, Ba and Rb would not be extracted to a separate solution; actinides are shown in red, lanthanides are shown in green; dissolution in 7000 L per T_{HM}; data based on Table 9 of report I-0963 [1].

Element	Mol·L ⁻¹	Element	Mol·L ⁻¹	Element	Mol·L ⁻¹
Zr	8.07E-03	Nd	6.05E-06	Actinides	1.78E-6
Mo	6.00E-03	I	6.76E-06	Lanthanides	1.33E-4
Cs	3.85E-03	Ce	3.69E-06	Other	2.50E-2
Ba	2.85E-03	In	2.89E-06		
Sr	1.84E-03	La	1.89E-06		
Pd	2.41E-03	Pr	1.69E-06		
Ru	2.40E-03	Pu	1.02E-06		
Rb	8.76E-04	Am	5.31E-07		
Te	8.23E-04	Tc	3.85E-07		
Rh	4.72E-04	Gd	2.21E-07		
Y	4.30E-04	Eu	1.84E-07		
Cd	1.99E-04	U	1.20E-07		
Ag	1.56E-04	Np	6.03E-08		
Se	1.46E-04	Cm	4.53E-08		
Sm	1.16E-04	Pm	1.74E-08		
Sn	1.09E-04	Tb	3.57E-09		
Br	5.56E-05	Dy	1.70E-09		
Sb	1.94E-05				

Figure 3 is a graphical presentation of the same data with a linear axis (top) and a logarithmic axis (bottom).

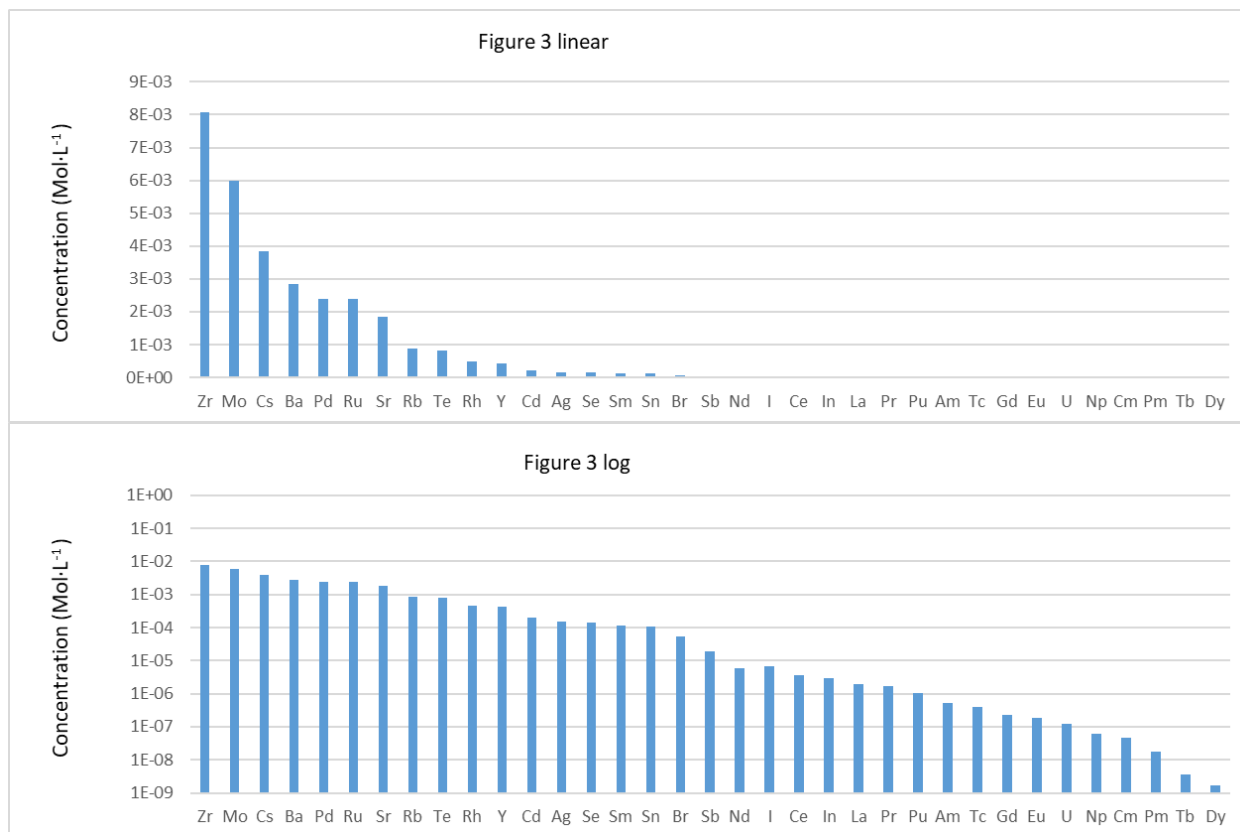


Figure 3: Radionuclide concentrations in DIAMEX raffinate, assuming Cs, Sr, Ba and Rb would not be extracted in a separate solution (top = linear scale, bottom is logarithmic scale); data based on Table 9 of report I-0963 [1]

The PUREX HAR in Figure 1 (HAR = High Activity Raffinate) also contains corrosion products, phosphorous and other chemicals, listed in Tables 7 and 8 from report I-0963 [1]. The data from these tables, converted into Mol·L⁻¹, are shown in Table 2. The phosphorous corresponds to the remainders of the tributyl phosphate of the extraction process, but it is likely that the organic compound will be destroyed by radiolysis. The remaining P fraction could be better characterized as phosphoric acid.

Table 2: Concentration of corrosion products, phosphorous and other impurities in the PUREX HAR solution; dissolution in 7000 L per T_{HM}; data based on Table 7 and 8 in report I-0963 [1].

Element	Mol·L ⁻¹
Fe	1.53E-02
Ni	2.33E-03
Cr	2.80E-03
P	1.68E-03
Cl	3.02E-04
F	2.82E-04
Na (+Al+K+Mg+Ca)	6.06E-04
Hf	6.00E-06
Zr	2.94E-03

So the DIAMEX raffinate contains both the radioisotopes given in Table 1 and the stable isotopes given in Table 2. There are two important assumptions related to the concentrations given in Table 2.

- In Table 9 of report I-0963 [1], the concentrations of the dissolved fuel elements are all given considering that a volume of 7000 L acid solution is used per ton uranium HM (= Heavy Metal). However, the concentrations for Fe, Ni, Cr and P in Table 7 of report I-0963 are given for 5000 L of solution per ton HM, and the concentration of the impurities in Table 8 of report I-0963 is given for 7500 L of solution per ton HM. For the calculations in Table 2, it is

assumed that the total amount of corrosion products and impurities would be the same if a volume of 7000 L per ton HM was used, but that the concentration would be lower by a factor 5000/7000 for the corrosion products, and higher by a factor 7500/7000 for the impurities. So the concentrations in Table 2 of this report have been calculated by multiplication of the concentrations in Tables 7 and 8 of report I-0963 with these factors.

- Table 8 of report I-0963 [1] gives the sum of the concentrations for Na, Al, K, Mg and Ca. It does not give the concentration for each element separately. For the calculation of the concentrations in Table 2, it is assumed that Na is the most abundant impurity, and the entire mass given in report I-0963 for Na, Al, K, Mg and Ca per liter of solution is assigned to Na. This decision is based on the data found in report UCRL-53326 [2], which describes the composition of the waste streams from commercial nuclear reactor fuel used for the production of SYNROC C. This report also mentions process chemicals, and gives a high concentration of Na, but no Al, K, Mg or Ca. Finally this will depend the purity of the chemicals that will be used during reprocessing.

3.2 Composition of the SANEX raffinate

The SANEX raffinate (based on Table 13 of report I-0963 [1]) would contain $1.36 \times 10^{-2} \text{ Mol}\cdot\text{L}^{-1}$ lanthanides (+yttrium) and $9.40 \times 10^{-8} \text{ Mol}\cdot\text{L}^{-1}$ minor actinides (Am and Cm). The detailed composition is given in Table 3.

Table 3: Radionuclide inventory of SANEX raffinate; dissolution in 7000 L per T_{HM} ; data based on Table 13 in report I-0963 [1].

Element	Mol·L ⁻¹	Element	Mol·L ⁻¹
Nd	6.04E-03	Am	5.31E-08
Ce	3.68E-03	Cm	4.09E-08
La	1.88E-03		
Sm	1.16E-03		
Y	6.41E-04		
Eu	1.83E-04		
Pm	1.73E-05		
Tb	3.55E-06		
Gd	2.19E-06		
Dy	1.69E-06		
Pr	1.69E-07		
Total Ln + Y	1.36E-02	Total Ac	9.40E-08

3.3 Composition of the curium solution

The curium raffinate solution (Table 22 of report I-0963 [1]) would contain $4.55 \times 10^{-5} \text{ Mol}\cdot\text{L}^{-1}$ Cm and still $3.2 \times 10^{-6} \text{ Mol}\cdot\text{L}^{-1}$ Am (Table 4).

Table 4: Radionuclide inventory of the curium solution; dissolution in 7000 L per T_{HM} ; data based on Table 22 in report I-0963 [1]; the data in report I-0963 were reported in Bq/L for each isotope and have been recalculated here to Mol·L⁻¹.

Element	Mol·L ⁻¹
Am	3.2E-06
Cm	4.55E-05

3.4 Composition of the mixed waste stream

Mixing the three waste streams will result in a dilution. The concentrations for the three waste streams (Table 1+ 2, Table 3, Table 4) are all calculated considering the use of 7000 L of solution per ton HM. This means that the total solution volume will be $3 \times 7000 \text{ L} = 21000 \text{ L}$, this is a dilution factor of 3. So, to calculate the concentration in this total volume, the concentrations given in Tables 1 – 4 are divided by a factor 3. The resulting composition is given in Table 5.

Table 5: Composition of the solution obtained by mixing the solutions of Tables 1+2, Table 3 and Table 4, considering the dilution factor 3.

Element	Mol·L ⁻¹	Element	Mol·L ⁻¹
Zr (FAP)	2.69E-03	I	2.25E-06
Nd	2.02E-03	Tb	1.18E-06
Mo	2.00E-03	In	9.64E-07
Cs	1.28E-03	Gd	8.05E-07
Ce	1.23E-03	Pr	6.19E-07
Ba	9.52E-04	Dy	5.65E-07
Pd	8.02E-04	Pu	3.42E-07
Ru	8.01E-04	Am	1.26E-06
La	6.27E-04	Tc	1.28E-07
Sr	6.13E-04	U	4.01E-08
Sm	4.25E-04	Cm	1.54E-05
Y	3.57E-04	Np	2.01E-08
Rb	2.92E-04	Fe	5.12E-03
Te	2.74E-04	Ni	7.77E-04
Rh	1.57E-04	Cr	9.32E-04
Cd	6.64E-05	P	5.60E-04
Eu	6.10E-05	Cl	1.01E-04
Ag	5.19E-05	F	9.40E-05
Se	4.85E-05	Na(+Al+K+Mg+Ca)	2.02E-04
Sn	3.62E-05	Hf	2.00E-06
Br	1.85E-05	Zr (impurity)	9.79E-04
Sb	6.46E-06	Zr (total)	3.67E-03
Pm	5.78E-06		

Cs, Sr, Ba and Rb are included in this table, but as they would be extracted to a separate solution, their concentrations in the mixed solution of Table 5 will be much lower. This is true also for Na, which is probably extracted together with the Cs and Sr.

For Zr, there is an important contribution from both the fuel dissolution, indicated as Zr(FAP), and an equally important contribution as an impurity, indicated as Zr(impurity). Table 5 also gives the sum of the two contributions, indicated as Zr(total). For the conditioning, only the chemical properties are important, so we should use the total Zr concentration. Figure 4 is a graphical presentation of Table 5.

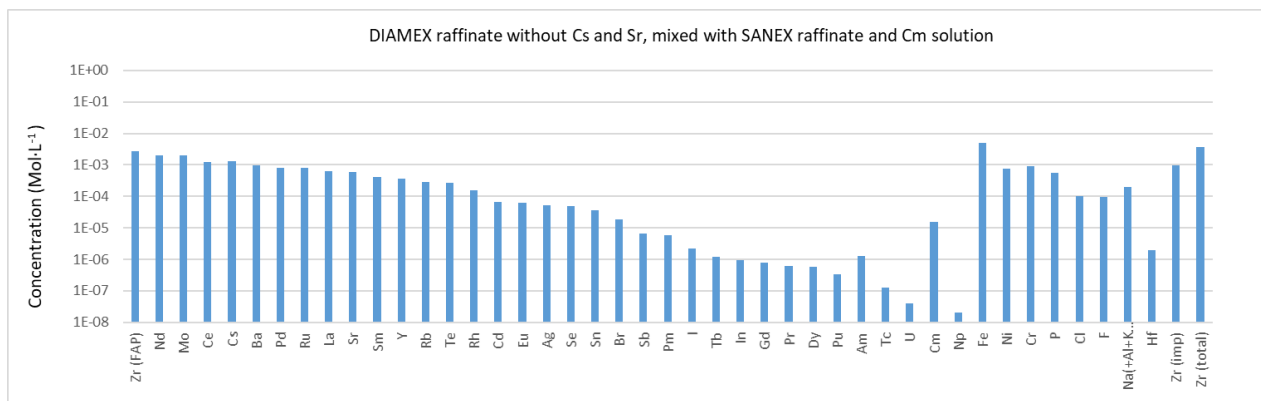


Figure 4: Composition of the solution obtained by mixing the solutions of Tables 1+2, Table 3 and Table 4, considering the dilution factor 3.

The following considerations are important for the interpretation of the data of Table 5:

- The HNO₃ concentration of the three waste streams is approximately 2.5 – 4 Mol·L⁻¹ for the DIAMEX raffinate, 1.25 Mol·L⁻¹ for the SANEX raffinate, and 2 Mol·L⁻¹ for the curium solution. The HNO₃ concentration of the mixed solution would thus be between $(2.5 + 1.25 + 2)/3 = 1.9 \text{ Mol}\cdot\text{L}^{-1}$ and $(4 + 1.25 + 2)/3 = 2.4 \text{ Mol}\cdot\text{L}^{-1}$.
- When the raffinate is stored, some of the components are likely to precipitate (Zr, Ag, Mo...). Hence the concentrations in Table 5 are high estimations of the dissolved concentrations.
- Hf and Ag are also found in the structural materials of the spent fuel assemblies. Control rods can contain Gd. It is not clear whether these will be part of the waste stream.²
- Not included are the organic molecules present in the DIAMEX raffinate, containing approximately 0.1 Mol·L⁻¹ oxalic acid and 0.01 – 0.03 Mol·L⁻¹ HEDTA. These concentrations will also be diluted by a factor 3 upon mixing. So the concentrations would be $0.1 / 3 = 0.033 \text{ M}$ oxalic acid and $0.03 / 3 = 0.01 \text{ M}$ HEDTA (we use the highest HEDTA concentration as the reference). The organic molecules will be subject to radiation and form radiolytical degradation products. HEDTA probably follows a similar decarboxylation reaction as it was identified for DTPA [3]. At higher pH absorption of radiation by water generates hydroxyl radicals that attack the C-COOH bond. The formed CO₂ is then removed from the system as it is a gas with limited solubility. In acidic solutions, the main radiolysis product is the hydrogen atom, which destroys the chelator. Nitric acid and water form H₂O₂ and HNO₂ upon irradiation. At higher dose rates, the oxalate is probably converted into carbonates and CO₂ gas. The degradation of tributyl phosphate (TBP) will likely generate phosphoric acid.

For the reference waste stream composition, we thus assume that the organic molecules will be destroyed by these radiolytical processes in the period of time during which the raffinates are stored awaiting further processing. Hence the organic molecules are omitted from the reference waste stream.

- The ratio between the various radionuclides is more relevant than the absolute concentrations for the purpose of this document. The mixed solution could be concentrated by evaporation (evaporation and denitration is often performed to limit the waste volume for temporary storage). This would increase all concentrations by the same factor, but the ratio would remain the same. Such pre-concentration is necessary for HIP-ing, where all water should be removed and only the dry residu is placed in the Hot Isostatic Press. But for geopolymerization this is not necessary, but it can be considered. Concentrating the solution will also decrease further the pH. If this is done at high temperature, the nitric acid will decompose in NO₂, H₂O and O₂.
- Although Table 5 assumes the mixing of the waste streams, all options (mixing or not) are open. The Tc raffinate is in the classical reprocessing waste treatment calcined and vitrified together with the PUREX HAR solution. In the advanced reprocessing scheme, it can also be mixed with the other waste streams, but the SCK report does not

² Hf and Ag originating from structural materials of spent fuel assemblies were not taken into account as we have no data. Table 8 in I-0963 contains Hf, however this is originating from the corrosion of the equipment used for reprocessing. The control rods were not taken into account, as we have obtained only information about the fuel composition and did not obtain info on the composition of the control rods and do not know how many control rods are in a fuel element. Furthermore, we do not know whether these control rods are also chopped and dissolved or whether these could be removed from the spent fuel elements before the fuel is chopped. In addition, sometimes extra neutron poisons are added (e.g. Gd) to the liquor to improve criticality safety. We have no detailed info from the existing commercial reprocessing plants. In addition, the situation might be different in a future plant.

give information about the expected Tc concentration in the Tc raffinate. Certainly, the low Tc concentration shown in Figure 3 will be much higher if the Tc raffinate is added.

- We consider only the corrosion products and impurities in the DIAMEX raffinate. We do not know if the SANEX raffinate and Cm solution will generate similar amounts of corrosion products and impurities. If that is the case, the dilution by factor 3 will underestimate the real concentrations in the mixture. It seems likely that most corrosion will occur in the fuel dissolution step, though.
- Some elements are dissolved only partly in the fuel dissolution and reprocessing. This is the case for Mo, Pd, Rh, Ru, Tc and Zr (see table 3 in report I-0963 [1]). This fraction can be separated and calcined to be vitrified together with the dissolved components. This fraction is not considered in the reference waste stream for ASOF.

4. Definition of the composition of the reference waste streams

4.1 General approach

The objective of ASOF WP3 is to develop and test novel waste matrices that can immobilize waste streams with a composition like the one given in Table 5. For this purpose, it is appropriate to simplify the complex reference waste stream, to have a simplified reference waste stream composition. Hence we define some simplification criteria.

4.2 Reference composition of the Cs and Sr waste stream

Cs and Sr are assumed to be separated from the first DIAMEX raffinate (see Figure 2). Ba (an earth alkali like Sr) and Rb (an alkali like Cs), and Na are assumed to be co-extracted with the Sr and Cs. This has an important effect on the waste loading, because the amount of Ba is larger than the amount of Sr in the DIAMEX raffinate (see Table 5). There are methods that can extract Cs and Sr simultaneously and methods that can extract them separately. Disposal of Cs and Sr in two different waste matrices would imply no cost saving. To maximally reduce the volume of conditioned waste, it would be better to immobilize Cs and Sr in the same matrix. This is our current reference scenario.

The Cs and Sr waste stream will be aqueous. The organic molecules will be destroyed by radiolysis. Because the composition of the solution used for the extraction is not yet defined, we consider only elements present in the DIAMEX raffinate. We assume it will be a 0.01 M HNO₃ solution. Assuming further that all Cs and Sr will be extracted from the DIAMEX raffinate with a very high recovery factor, together with all the Ba, Rb and Na, the molar concentrations of Table 1 (Cs, Sr, Ba, Rb) and Table 2 (Na) can be used to estimate the composition of the Cs and Sr waste stream. These are summarized in Table 6. Because we do not know the dilution, the absolute concentrations will be different, but the ratios between the solutes should remain the same.

Table 6: Preliminary composition of the Cs/Sr reference solution.

Element	Mol·L ⁻¹
Cs	3.85E-03
Sr	1.84E-03
Ba	2.85E-03
Rb	8.76E-04
Na	6.06E-04

4.3 Reference composition of rest waste stream

The rest waste stream will include all components of Table 5, except those included in the Cs and Sr waste stream. For the simplification of the composition of the reference waste solution, elements with low concentration are omitted or represented by a similar element with a higher concentration.

- The Cs, Sr, Ba, and Rb remaining in the rest waste stream is neglected.
- Na is expected to be co-extracted with the Cs, but because there is little information about this, Na is kept also in the reference composition of the rest waste stream. The Na is thus considered in both waste streams. This makes the immobilization more challenging, and can thus be seen as a conservative approach.
- Elements in Table 5 with concentrations lower than 10⁻⁴ Mol·L⁻¹ are omitted. Hence the reference composition does not include any Sb, Pm, Tb, I, Tb, In, Gd, Pr, Dy, Pu, Am, Tc, U, Np, Hf, Ag, Cd, Sn or Se.
- From the lanthanide group only Nd is added (the most abundant). The Nd represents the sum of Nd, Ce, La, Sm, Eu, Pm, Tb, Gd, Pr, Dy and Y. Nd is used also to represent Cm, which is in the trivalent state, just as the lanthanides. The concentration of Nd in the reference medium is determined as the sum of the concentrations of all these elements in Table 5.
- From the halogen group Cl, F, Br and I are present, but because Cl is the most abundant element, and because of the safety issues related to the use of F, we use Cl to represent the whole group.
- The other components with concentrations > 10⁻⁴ Mol·L⁻¹ are considered for the reference solution.

The elements considered in the rest waste stream (and their likely valency in the solution) are thus :

- Fe(III), Cr(III), Ni(II) (= corrosion products from the PUREX HAR)
- Na, representing Na + Al + K + Mg + Ca from the PUREX HAR
- Zr(IV) from the dissolved fuel and as an impurity
- Nd(III) representing all lanthanides + Y + Cm
- Te (IV), Mo(IV)
- Rh(III), Pd(II), Ru. For Ru the speciation is very complicated, but Ru(III) is assumed to be present.
- Cl⁻
- P (phosphoric acid)

The resulting composition is given in Table 7. As mentioned in section 3.4, the undissolved fraction of Zr, Mo, Ru, Rh and Pd is not considered in the reference waste stream.

Table 7: Reference composition of the rest waste steam.

Element	Reference Concentration in Mol·L ⁻¹
Fe	5.12E-03
Nd (representing lanthanides, Y, Cm)	4.74E-03
Zr(total)	3.67E-03
Mo	2.00E-03
Cr	9.32E-04
Pd	8.02E-04
Ru	8.01E-04
Ni	7.77E-04
Te	2.74E-04
Na (representing also Al, K, Mg, Ca)	2.02E-4
Rh	1.57E-04
Cl (representing Cl, F, Br, I)	2.00E-4
P (phosphoric acid)	5.6E-4

Comments

- The valencies assumed for the waste components, are those expected in the raffinates. These valencies can change in the conditioning process by changes of pH and/or redox conditions. This is very likely for the ceramic waste form produced by HIP-ing, where reducing conditions can be imposed. This can have as a consequence that elements that are in ionic form in the initial solution, are present as metals (0) in the ceramic. This can be the case for Ru, Mo, Ni, Pd, Rh, Te, and part of the Fe (and for Tc and S, but these are not considered in the reference medium).
- Actinides (Pu, U and Np) are not considered in the reference composition. Their total concentration is very low. We might add U if we want to follow the release of this group, but the concentrations may be too low to be detectable, and it will make the samples 'active'.
- Although Se, I and Tc are not considered in the reference composition because of their low concentration in the raffinate, they are important for the safety of the disposal. This is the case also for Cl³⁶. C¹⁴ would be found in the off-gases, but it is not clear if these are recycled somewhere. For the current experimental program, these components will not be studied.

5. Conclusions and perspectives

The reference compositions given in Tables 6 and Table 7 will be used for the preparation of simulated waste forms whose chemical durability will be tested. These will be ceramics and geopolymers. Whether or not the complete list of components will be added, is an evaluation that will be made by the laboratories that prepare the test samples.

6. References

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