GENIORS

Research and Innovation Action (RIA)

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Report with collected data on the main solvents and the density laws build

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Summary

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Approval

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GENIORS
GEN IV integrated oxide fuels recycling strategies

IRSN
INSTITUT DE RADIOPROTECTION
ET DE SÛRETÉ NUCLÉAIRE

PROJET GENIORS

DATA NECESSARY FOR THE ESTABLISHMENT OF DENSITY LAWS FOR NUCLEAR CRITICALITY SAFETY IN THE FRAMEWORK OF THE EURO-GANEX PROJECT

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Rapport n°2020-00804

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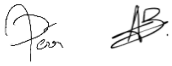
Visa					

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RÉSUMÉ

Mots clés : *données, EURO-GANEX, GENIORS, Solvants*

Le projet GENIORS s'intéresse à la détermination de nouveaux procédés d'extraction d'éléments fissiles dans le cadre du retraitement des nouvelles gestions de combustibles. Jusqu'à présent, la démonstration de sûreté a été effectuée en utilisant de l'eau comme solvant, en postulant que le choix de l'eau était conservatif. Le but du présent travail est de construire des lois de densité pour d'autres solvants utilisés dans les nouveaux procédés et dans un autre rapport, de vérifier si le choix de l'eau est ou non conservatif par rapport à eux.

Ce rapport fait partie du livrable D9.2 (workpackage 9) du projet GENIORS. Il décrit une méthodologie pour établir des lois de densité pour les éléments fissiles impliqués dans les solvants EURO-GANEX et présente les données collectées pour établir une telle loi de densité. Cette tâche s'inscrit dans le cadre du projet GENIORS [1], qui est un projet européen dédié à la gestion du combustible nucléaire pour les cycles futurs. Il devrait fournir à l'UE des stratégies fondées sur la science pour la gestion du combustible nucléaire et contribuer de manière significative à son indépendance énergétique. À plus long terme, les résultats du projet faciliteront la gestion des déchets radioactifs en réduisant leur volume et leur radio-toxicité, et favoriseront une utilisation plus efficace des ressources naturelles.

Dans une première partie, nous décrirons pourquoi les lois de densité sont nécessaires en sûreté-criticité et à quoi elles ressemblent. Ensuite, nous nous concentrerons sur la stratégie d'établissement de lois de densité impliquant de nouveaux solvants.

Enfin, les données collectées seront présentées.

SUMMARY

Key-words : *data, EURO-GANEX, GENIORS, Solvents*

The GENIORS project is focused on the determination of new processes for extraction of fissile species in the framework of the reprocessing of new fuel managements. Up to now, the safety demonstration was performed using water as a solvent, postulating that water was conservative. The aim of the present work is to build density laws for other solvents used in the new processes and in a further report, to check whether or not water is conservative when compared to them.

This report is part of the D9.2 deliverable (working package 9) of the GENIORS Project. It describes a methodology for establishing density laws for fissile species involved in EURO-GANEX solvents and presents the data collected for establishing such density law. This task takes part into the GENIORS Project [1], which is a European project dedicated to the management of nuclear fuel for future cycles. It is expected to provide the EU with science-based strategies for nuclear fuel management and contribute significantly to its energy independence. In the longer term, the project's results will facilitate radioactive waste management by reducing its volume and radiotoxicity, and support a more efficient utilisation of natural resources.

In a first part, we will describe why density laws are needed in criticality safety and what they look like. Then, we will focus on the strategy to establish density laws involving new solvents.

Finally, the collected data will be presented.

GENIORS

GEN IV integrated oxide fuels recycling strategies

Data necessary for the establishment of density laws for Nuclear Criticality Safety in the framework of the EURO-GANEX Project

Author(s): Nicolas Leclaire (Institut de radioprotection et de Sûreté Nucléaire)

Version: 1 issued on 11/06/2020

CONTENT

This project has received funding from the EURATOM research and training programme 2014-2018 under grant agreement No 755171. The content of this deliverable reflects only the author's view. The European Commission is not responsible for any use that may be made of the information it contains.

1. INTRODUCTION

The GENIORS project is focused on the determination of new processes for extraction of fissile species in the framework of the reprocessing of new fuel managements. Up to now, the safety demonstration was performed using water as a solvent, postulating that water was conservative. The aim of the present work is to build density laws for other solvents used in the new processes and in a further report, to check whether or not water is conservative when compared to them.

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In a first part, we will describe why density laws are needed in criticality safety and what they look like. Then, we will focus on the strategy to establish density laws involving new solvents.

Finally, the collected data will be presented.

2. DEFINITION OF A DENSITY LAW

Density laws are intimately linked to the French criticality safety practice. Indeed, in French criticality safety studies, the bulk density of solutions is rarely known. One only has access to the concentration in the main specie (fissile very often), the acidity and the temperature. Density laws are used to determine the bulk density of the solution and then have access to the solvent content.

They take the shape of mathematical relationships linking concentration, acidity and temperature to the density or to the moderation ratio (H/X where X is the atomic concentration in fissile specie and H the atomic concentration in hydrogen).

$$\rho = f(C(X), \text{Acidity}, T°C) \quad (1)$$

Different types of density laws exist:

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- Theoretical ones,
- Experimental ones,
- Semi empirical ones.

The choice of the density law is intimately linked to the conservatism associated with a criticality study.

In fact, k_{eff} $\left(k_{eff} = \frac{\nu\times\Sigma_{eff}}{\Sigma_a + Leakages}\right)$, which is the main physical parameter in criticality, is the ratio of the production of neutrons ($\nu\Sigma_{eff}$) versus the absorption (Σ_a) and leakages from the system and characterizes the propensity of a chain reaction to self-sustain. Then, the higher the density, the lower the leakages and, at fixed concentration in fissile specie, the higher the moderation of neutrons. Consequently, maximizing the density leads to an increase of reactivity.

A scale of conservatism for density laws can be established versus the density of the electrolyte corresponding with the fissile specie and the density of the solvent. The higher the electrolyte density, the more conservative the density law is.

2.1. THEORETICAL DENSITY LAWS

Theoretical density laws are used to “cover” fictitious fissile media, for instance metallic uranium in solution. They are voluntarily conservative and are based on the volume additive principle consisting in saying that the volume of a solution is the sum of the solute volume and the solvent one, which remains true as long as the concentration in fissile specie remains low and the interactions between molecules of solute remain limited.

2.2. EXPERIMENTAL DENSITY LAWS

Experimental density laws correspond to a really existing mixture. They are based on experimental measurements. And interpolations are performed between various measurements. They are used for uranium oxifluoride for instance.

2.3. SEMI EMPIRICAL DENSITY LAWS

Semi-empirical density laws use measurement values and a physical model that postulates the values of densities at concentration different from the ones corresponding to the measurement points.

They are used for uranium uranyl nitrate, plutonium nitrate for instance.

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3. STRATEGY TO ELABORATE THE DENSITY LAW

3.1. METHODOLOGY

A first methodology based on the volume addition of mixtures having the same solvent activity was investigated ("isopiestic" concept) [2, 3]. The idea was to apply the same methodology as for mixtures involving nitrates. Such works were based on PhD results obtained before 2000 by Nicolas Charrin [4] at CEA Marcoule. These works were realized within collaboration between INSTN Saclay and CEA Marcoule. However, discussions with French and international experts (Jean-Pierre Simonin from CNRS and Philippe Guilbaud from CEA) during the GENIORS meetings showed that measurements of organic solvents activities proved to be really tough if not impossible. As a result and given that the range of concentrations in fissile species of the process was limited to relatively low concentrations (< 150 g/L), a standard volume additive law could be envisioned, without deviating so much from a theoretical behaviour. This methodology was therefore selected for the realization of criticality standards calculations.

3.2. VOLUME ADDITIVE LAW

The volume additive principle consists in postulating that the volume of a mixture is the sum of the volumes of each constituent: fissile species (solute), acid and solvent (extractant + diluent).

It is always true at low concentrations since low molecular interactions are observed. However, the rule is less and less followed while the solute concentration increases. A volume contraction, due to specific interaction between the solute and the solvent, can occur and leads to higher densities than expected.

3.2.1. GANEX 1ST STEP

In the first step of the GANEX process [5], the separation of uranium and plutonium is at stake. As illustrated in Figure 1, the process is fed with 103 g/L of uranium, traces of Tc and Np and 22.7 g/L of plutonium in 5 mol/L of nitric acid. The plutonium along with neptunium, americium and lanthanides are extracted in the solvent (extractant and diluent) and uranium remains in the water part. DEHIBA is used as the extractant and TPH behaves as the diluent.

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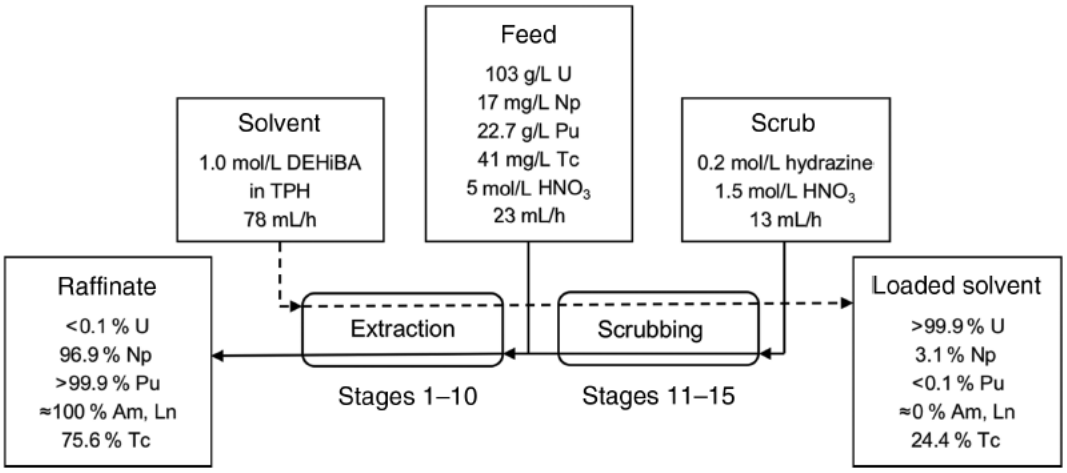

Figure 1: GANEX 1st step process.

For the purpose of our study, nitric acid will be first neglected since it contributes to decrease the reactivity as, for the same concentration in fissile specie, it decreases the number of water molecules and adds more nitrogen, which is a neutron absorber. The plutonium weight isotopic vector is a vector traditionally used in French criticality studies to bound plutonium media encountered in the nuclear fuel cycle. It is the following: 71 wt% ^{239}Pu, 17 wt% ^{240}Pu, 11 wt% ^{241}Pu and 1 wt% ^{242}Pu. This choice is purely arbitrary but we need to fix an isotopic vector to make a comparison. In the next deliverable, this assumption will be evaluated in terms of criticality-safety comparing with a more realistic isotopic vector that is representative of burnt fuel.

Uranium is assumed to be close to natural uranium with an enrichment of 0.7 %. Room temperature (20 °C) is retained.

The density of the solution is calculated using formula (1).

The density of the extractant-diluent (DEHIBA-TPH) is calculated using formula (2).

$$\rho_{solution} = C(UO_2(NO_3)_2) + C(Pu(NO_3)_4) + \rho_{extractant-diluent} \times \left(1 - \frac{C(U)}{\rho(U)} - \frac{C(Pu)}{\rho(Pu)}\right) \quad (1)$$

$$\rho_{extractant-diluent} = \left(C(extractant) + \rho_{diluent} \times \left(1 - \frac{C(extractant)}{\rho_{extractant}}\right)\right) - 0.00072 \times (T - 25) \quad (2)$$

With C(extractant), the concentration in DEHIBA in g/cm^3, $\rho_{diluent}$ being the density of TPH at 25 °C.

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T is the temperature en °C.

$\rho_{extractant}$ is the density of DEHIBA at 25 °C.

It should be noted that the molarity in extractant is assumed to be constant and equal to 1 mol/L.

3.2.2. GANEX 2ND PART

In the second step of the GANEX process [5], uranium has been separated from plutonium. As illustrated in Figure 2, the process is fed with 10 g/L of plutonium in 5.9 mol/L of nitric acid and 0.055 mol/L of CDTA (trans-1,2-cyclohexanediaminetetraacetic acid). In this step of the process, plutonium is separated from neptunium, americium and lanthanids.

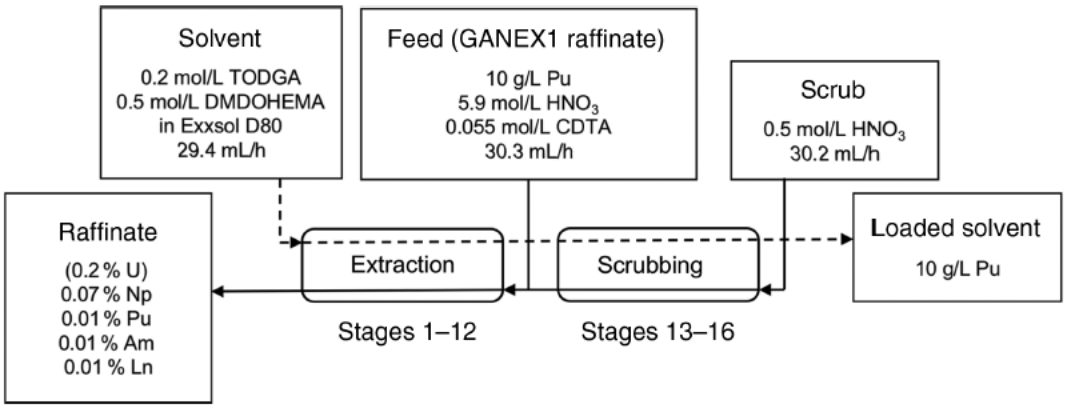

Figure 2: GANEX 2nd step process.

Once again, for the purpose of our study, nitric acid will be first neglected since it contributes to decrease the reactivity. The plutonium weight isotopic vector is a vector traditionally used in French criticality studies to bound plutonium media encountered in the nuclear fuel cycle. It is the following: 71 wt% ^{239}Pu, 17 wt% ^{240}Pu, 11 wt% ^{241}Pu and 1 wt% ^{242}Pu.

Room temperature (20 °C) is retained.

Uranium and CDTA will be neglected since their content is very low. Neglecting uranium contributes to an increase of reactivity since plutonium is more conservative than uranium in terms of criticality.

The density of the solution is calculated using formula (3).

The density of the extractant-diluent (TODGA/DMDOHEMA-EXXSOL) is calculated using formula (4).

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$$\rho_{solution} = C(Pu(NO_3)_4) + \rho_{extractant-diluent} \times \left(1 - \frac{C(Pu)}{\rho(Pu)}\right) \quad (3)$$

$$\rho_{extractant-diluent} = \left(C(TODGA) + C(DMDOHEMA) + \rho_{diluent} \times \left(1 - \frac{C(TODGA)}{\rho(TODGA)} - \frac{C(DMDOHEMA)}{\rho(DMDOHEMA)}\right)\right) \quad (4)$$

With $\rho_{diluent}$ being the density of EXXSOL in g/cm^3 at the desired temperature in °C.

T is the temperature in °C.

$\rho_{extractant-diluent}$ is the density of the solvent in g/cm^3 at 20 °C.

$C(TODGA)$ is the concentration of TODGA in g/cm^3.

$C(DMDOHEMA)$ is the concentration of DMDOHEMA in g/cm^3.

$\rho(TODGA)$ is the density of TODGA at the desired temperature in g/cm^3.

$\rho(DMDOHEMA)$ is the density of DMDOHEMA at the desired temperature in g/cm^3.

It should be noted that the molarity in TODGA and DMDOHEMA is assumed to be constant and equal respectively to 0.2 mol/L and 0.5 mol/L.

3.2.2. GANEX 3RD STEP

In the third step of the GANEX process [5], uranium has been separated from plutonium. As illustrated in Figure 3, the process is fed with 10 g/L of plutonium in 0.5 mol/L of nitric acid and 0.055 mol/L of SO_3-Ph-BTP and 1 mol/L of AHA. In this step of the process, a more achieved separation is performed to set apart lanthanides from other constituents.

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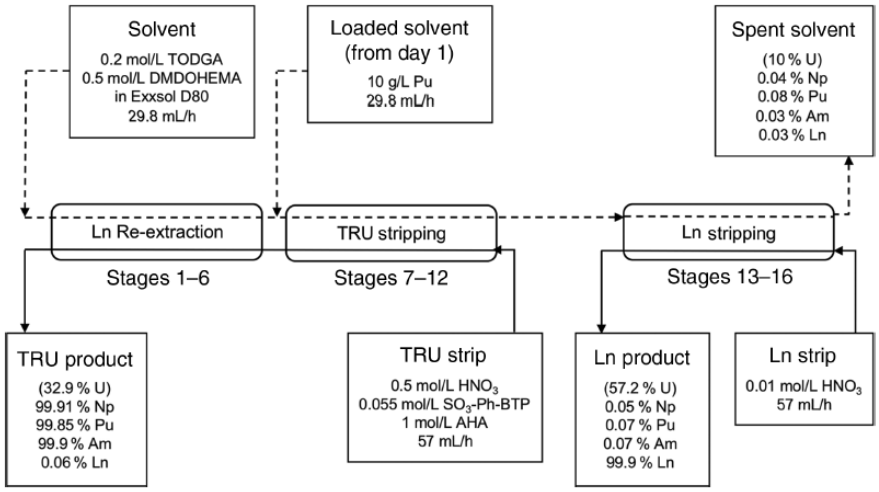

Figure 3: GANEX 3rd step process.

Contrary to the previous step, nitric acid has not been neglected in a first approach. The isotopic vector of plutonium is a vector traditionally used in criticality to bound plutonium media encountered in the nuclear fuel cycle. It is the following: 71 wt% ^{239}Pu, 17 wt% ^{240}Pu, 11 wt% ^{241}Pu, 1 wt% ^{242}Pu.

Room temperature (20 °C) is retained.

Uranium will be neglected since its content is very low. Neglecting uranium contributes to an increase of reactivity since plutonium is more conservative than uranium in terms of criticality.

The density of the solution is calculated using formula (3).

The density of the extractant-diluent (AHA/SO_3Ph-BTP/water) is calculated using formula (4).

$$\rho_{solution} = C(Pu(NO_3)_4) + C(HNO_3) + \rho_{extractant-diluent} \times \left(1 - \frac{C(Pu)}{\rho(Pu)} - V(HNO_3) \times 0.001 \times H^+\right) \quad (3)$$

$$\rho_{extractant-diluent} = \left(C(AHA) + C(SO_3 - Ph - BTP) + \rho_{diluent} \times \left(1 - \frac{C(AHA)}{\rho(AHA)} - \frac{C(SO_3-Ph-BTP)}{\rho(SO_3-Ph-BTP)}\right)\right) \quad (4)$$

With $\rho_{diluent}$ being the density of water at the desired temperature (T).

T is the temperature in °C.

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$\rho_{extractant-diluent}$ is the density of the solvent at 20 °C.

V(HNO_3) is the molar volume of acid in cm^3/mol.

$C(AHA)$ is the concentration of AHA in g/cm^3.

C(HNO_3) is the concentration of HNO_3 in g/cm^3 and H^+ is the acidity in mol/L.

$C(SO_3 - Ph - BTP)$ is the concentration of $SO_3 - Ph - BTP$ in g/cm^3.

$\rho(AHA)$ is the density of AHA at 20 °C in g/cm^3.

$\rho(SO_3 - Ph - BTP)$ is the density of $SO_3 - Ph - BTP$ at 20 °C in g/cm^3.

The density of the extractant-diluent at a temperature different from room temperature has been obtained experimentally through a linear formula (5). It allows checking the results of formula (4).

$$\rho_{extractant-diluent}(T) = -0.000388678 \times T + 1.0641 \quad (5)$$

3.3. LIMITATIONS

It should be noted that actinides and fission products are involved in some of the steps of the GENIORS project. However, even if it would have been possible to do it, they have not been taken into account in the building of the volume additive laws based on the new solvents. The reason is that the quantities in these species is often low and regarding the fission products, as they absorb neutrons they contribute to a decrease of k_{eff}. Anyway, the behavior of the solvent regarding k_{eff} will not be drastically modified by their presence. If water is conservative for a solution of plutonium when compared to the GENIORS solvents, it will remain conservative with a small quantity of actinides and fission products.

3.4. DATA COLLECTED

To establish density laws, one needs to know precisely the main characteristics of the extractants/diluents that make the solvent and especially their proportions and bulk densities versus temperature. Such data were not available at IRSN. As a consequence, a request was made to the GENIORS group and the data were provided by members of the GENIORS Project under the auspices of Andrea Geist to whom IRSN is grateful.

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3.4.1. DENSITY OF SOLVENTS

The majority of extractants/diluents densities were found in the literature or were provided by participants to the GENIORS project. All these data are gathered in Table 1.

Table 1: Main characteristics of solvents and behaviour versus temperature

Extractant/diluent	Reference concentration of extractant in diluent (mol/L)	Density in g/cm^3		Chemical formula	Behaviour versus temperature in °C	Reference
TPH		0.7551 (25 °C)		$C_{12}H_{26}$	0.7551 × (1-0.0009826 × (T-25))	Data from Christian Sorel (see The data are gathered in Table 2. Table 2)
DEHIBA	1.151	0.8638 (25 °C)		$C_{20}H_{41}NO$	-0.00066× (T-25) + 0.8638	PhD works [6]
EXXSOL		0.798 (15 °C)	0.684	n-heptane - C_7H_{16}	-0.00068 × (T-15) + ρ (15 °C)	Analogy with TODGA/DMDOHEMA behaviour)
			0.7786	cyclohexane C_6H_{12}		
			0.6594	n-hexane C_6H_{14}		
			0.77	methylcyclohexane C_7H_{14}		
TODGA	0.2	0.9054 (25 °C)		$C_{36}H_{72}N_2O_3$	-0.00066 × T + 0.9219	Data from Justine Cambe-Issaadi, Anne Lélias (CEA) (See Table 3)
DMDOHEMA	0.5	0.914 (25 °C)		$C_{29}H_{58}N_2O_3$	-0.00068 × T + 0.931	
AHA	1	1.2837		$C_2H_5O_2N$	$-0.000388678 \times T + 1.0641$	Recalculated
SO_3-Ph-BTP	0.055	1.842 (inferred from calculation)		$C_{35}H_{19}S_4O_{12}Na_4N_7$		Recalculated

Density of organic solutions involved in the GANEX 1st cycle have been measured in order to estimate flowrates variations with composition and temperature in the simulation code PAREX. In addition, the knowledge of the organic density is useful to convert organic

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concentration from the molarity scale (mol/L) to the molality scale (mol/kg) which is retained for the modelling of extraction and complexation equilibria in our code. All the density data have been measured with an Anton-Paar density meter.

Density of TPH has been measured on the temperature range 20-60°C.

The data are gathered in Table 2.

Table 2: Density of DEHIBA solution versus temperature.

[DEHiBA] (mol/l)	T (°C)	ρ_{exp} (g/ml)
1.49	25	0.8137
1.49	35	0.8065
1.49	45	0.7991
0.99	25	0.7949
0.99	35	0.7877
0.99	45	0.7805

From these data, it is possible to establish the behavior of the density versus temperature as it is given in Table 1.

Regarding the GANEX 2nd step, acquisition of densities of the pure TODGA and DMDOHEMA was performed from 15 to 55°C, using a SVM 3000 densimeter (ANTON PAAR). Justine Cambe-Issaadi and Anne Lélias (CEA) provided the data to IRSN. Each data is the mean value of two measurements and is reported in Table 3.

From these data, it is possible to establish the behavior of the density versus temperature as it is given in Table 1.

Table 3: Measurement of TODGA and DMDOHEMA densities versus temperature.

	Density (g/cm^3) ± 0.0002 g/cm^3	
T (°C)	TODGA	DMDOHEMA
55	0.8857	0.8936
45	0.8923	0.9005
35	0.8988	0.9072
25	0.9053	0.914
15	0.9120	0.9208

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Regarding the GANEX 3rd phase, crystal densities of AHA and SO_3-Ph-BTP were not provided. However, measurements were performed on solutions of 1mol/L of AHA and on solutions of 1 mol/L of AHA + 0.055 mol/L of SO_3-Ph-BTP (see Figure 4 and Figure 5). From these measurements, one can derive the crystal densities of AHA and SO_3-Ph-BTP, which are respectively determined as 1.2837 g/cm^3 and 1.842 g/cm^3.

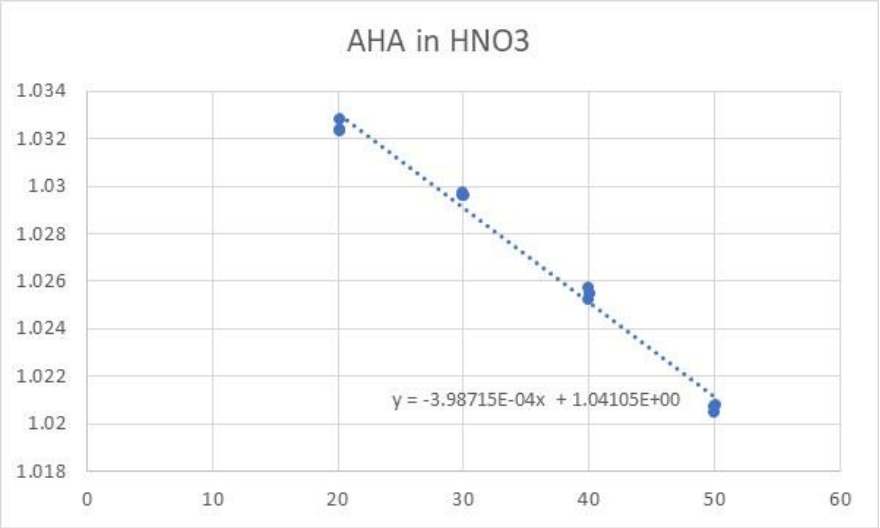

Figure 4: Measurement of a solution of 1 mol/L AHA.

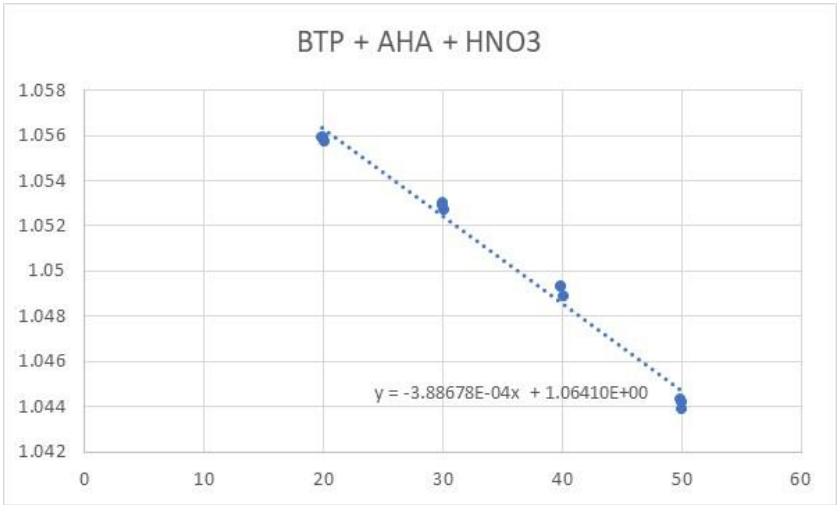

Figure 5: Measurement of a solution of 1 mol/L AHA + 0.055 mol/L SO_3-Ph-BTP.

From these data, it is possible to establish the behavior of the density versus temperature as it is given in Table 1.

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3.4.2. VALIDATION OF THE SOLVENTS DENSITIES

Comparisons of densities calculated using the volume additive formula and measured densities are necessary to validate the established density laws.

3.4.2.1 VALIDATION OF THE SOLUTIONS WITH DEHIBA

Density measurements of organic solutions containing both nitric acid and uranyl nitrate have been measured at 25°C after a counter-current trial performed in mixer-settlers. These measurements were reported by Christian Sorel from CEA and are given in Table 4.

One can see that the difference of bulk density between measured densities and calculated densities is always lower than 2 %, which indicates that the volume addition law density correctly predicts the behaviour of the density trend. Moreover, except for the first sample (concentration in U(VI) equal to 0.009 g/L), the calculated density is always higher than the measured one, which is conservative from the criticality-safety point of view.

Table 4: Measurements of organic solutions with DEHIBA and an extractant.

[DEHiBA] concentration (mol/L)	$[HNO_3]$org, exp (mol/L)	[U(VI)]org, exp (g/l)	Measured density (ρ exp) (g/ml)	Calculated density (ρ calc)	Difference (%)
1.151	0.2	0.009	0.8121	0.8069	-0.6403
	0.69	0.01	0.8183	0.8252	0.8432
	0.78	0.077	0.8212	0.8287	0.9133
	0.81	0.41	0.8227	0.8303	0.9238
	0.79	2.02	0.8253	0.8320	0.8118
	0.74	10.27	0.8333	0.8426	1.1160
	0.62	34.05	0.8614	0.8739	1.4511
	0.41	64.95	0.8987	0.9127	1.5578
	0.41	55.45	0.8842	0.8983	1.5947
	0.36	58.06	0.886	0.9004	1.6253
	0.31	60.56	0.8868	0.9023	1.7479
	0.27	61.39	0.8874	0.9022	1.6678
	0.23	61.2	0.8866	0.9003	1.5452
	0.2	61.72	0.8865	0.9000	1.5228
	0.18	58.77	0.8815	0.8947	1.4974
	0.16	48.88	0.8672	0.8791	1.3665

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[DEHiBA] concentration (mol/L)	$[HNO_3]$org, exp (mol/L)	[U(VI)]org, exp (g/l)	Measured density (ρ exp) (g/ml)	Calculated density (ρ calc)	Difference (%)
	0.026	28.48	0.8347	0.8434	1.0423
	0.005	8.24	0.8055	0.8112	0.7076

3.4.2.2 VALIDATION OF THE TODGA+DMDOHEMA DENSITY

The GANEX 2nd step solvent density (0.2 mol/L TODGA + 0.5 mol/L DMDOHEMA) was also measured by classical methods as being 0.846 ± 0.003 mg/L at room temperature, by Galan Montano, Hitos from CIEMAT.

Using the bulk densities of the diluent and extractant determined previously (Table 3), one finds the value of 0.8435 g/cm^3 at room temperature. This value is consistent with the measured one.

3.4.2.3 VALIDATION OF THE SOLUTIONS WITH TODGA+DMDOHEMA IN EXXSOL

Density data for TODGA + DMDOHEMA in Exxsol D80, EURO-GANEX organic phase, has been acquired by Lancaster University for the GENIORS programme (Alexander Jackson, Michael Bromley, Colin Boxall (University Lancaster)).

Density data (at the lab temperature of 14.5 ± 0.5 °C) of the pure TODGA and DMDOHEMA was used in solution preparation to accurately make up 5.5cm^3 of 0.2mol/L TODGA + 0.5mol.dm^{-3} DMDOHEMA in Exxsol D80. A 5cm^3 BRAND BLAUBRAND density bottle was used to measure the density of the solution and errors were calculated from the tolerance of the thermometer and the density bottle. Error in the concentration of the TODGA and DMDOHEMA in solution was calculated from the tolerance of the 2 cm^3 glass pipette used in liquid transfer and volume measurement. Density as a function of temperature is shown in Table **5** and Figure 6.

Table 5: Density of 0.200 ± 0.006 mol/L TODGA and 0.500 ± 0.007 mol/L DMDOHEMA in Exxsol D80 from 20 to 60 °C.

T (°C) ± 0.5°C	Density (g/cm^3)
59.5	0.8141 ± 0.0016
43.0	0.8242 ± 0.0017

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T (°C) ± 0.5°C	Density (g/cm^3)
37.0	0.8300 ± 0.0017
30.5	0.8345 ± 0.0017
24.0	0.8387 ± 0.0017
20.0	0.8422 ± 0.0017

Density decreases linearly with temperature as shown in Figure 6.

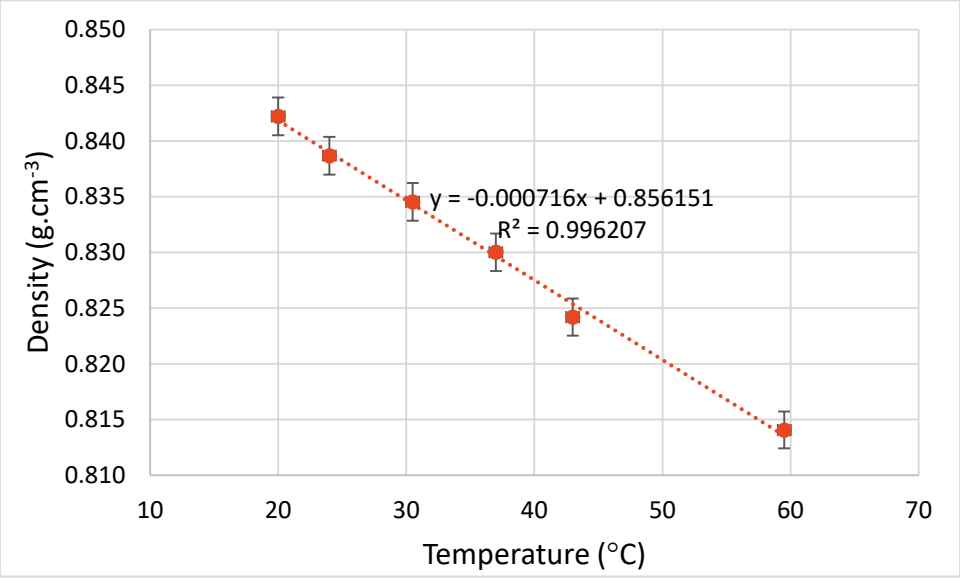

Figure 6: graph of density of 0.200 ± 0.006 mol/L TODGA and 0.500 ± 0.007 mol/L DMDOHEMA in Exxsol D80 from 20 to 60 °C.

4. CONCLUSION

Density data of diluents and extractants acting as solvents for the various steps of the GENIORS process were gathered with the help of the GENIORS partners. In this deliverable, IRSN proposes a methodology for establishing density of mixtures based on the volume additive principle. This methodology is justified for the concentrations encountered in the GENIORS process. Further comparison will be made between the density laws built using this methodology and the solvents of the various steps of the GENIORS process and a volume additive law using water as a moderator. The objective is to check that water is still bounding in terms of criticality-safety.

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6. APPENDIX

The aim of this appendix is to show how to determine numerically the density of the solution with the formulas given in the report and the data collected. This exercise is done with solutions of the first step of the GENIORS process.

In the first step of the process, the extractant is DEHIBA and the diluent TPH.

The below formulas, given in the report, are used for the calculation.

$$\rho_{solution} = C(UO_2(NO_3)_2) + C(Pu(NO_3)_4) + \rho_{extractant-diluent} \times \left(1 - \frac{C(U)}{\rho(U)} - \frac{C(Pu)}{\rho(Pu)}\right) \quad (1)$$

$$\rho_{extractant-diluent} = \left(C(extractant) + \rho_{diluent} \times \left(1 - \frac{C(extractant)}{\rho(extractant)}\right)\right) - 0.00072 \times (T - 25) \quad (2)$$

- **Data available (*see Table 1*):**

At 25 °C, the density of TPH is 0.7551 g/cm^3 so $\rho_{diluent}$ = 0.7551 g/cm^3. M_{THP} = 170.337 g/mol.

At 25 °C, the density of DEHIBA is 0.8638 g/cm^3, so $\rho(extractant)$ = 0.8638 g/cm^3. M_{DEHIBA} = 311.55 g/mol.

The concentration of extractant in the solvent is 1.151 mol/L, so $C(extractant)$ = 1.151 mol/L = 0.35859 g/cm^3 with M_{DEHIBA} = 311.55 g/mol.

- **Calculation of density of solution:**

Using the previous data and formula (*2*), we obtain $\rho_{extractant-diluent}$ **=0.80022 g/cm^3**.

- **Calculation of density of solution:**

The ratio in weight of plutonium (Pu/UPu) in the first step of the process is 18.05887 %, since the concentration in Pu is assumed to be 22.7 g/L and that in uranium 103 g/L (*see flowsheet Figure 1*).

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If we assume a concentration in uranium of 103 g/L, the concentration in plutonium is 22.7 g/L. The isotopic vector of plutonium in wt. % is assumed to be 71/17/11/1 % for the exercice.

$\boldsymbol{\rho(U)}$ **= 1.3306 g/cm³** since the density of U in $UO_2(NO_3)_2$-6 H_2O crystal is 2.8 g/cm³ [7]. Indeed, $(\rho(U) = d_{crystal} \times {M_u}/{M_{crystal}})$

$\boldsymbol{\rho(Pu)}$ **= 1.2024 g/cm³** since the density of $Pu(NO_3)_4$-5 H_2O crystal is 2.9 g/cm³ [7].

$$\Downarrow$$

$$C(UO_2(NO_3)_2) = C(U) \times M(UO_2(NO_3)_2)$$

$$C(Pu(NO_3)_4) = C(Pu) \times M(Pu(NO_3)_4)$$

With $M_{UO_2(NO_3)_2}$M = 394.0350 g/mol and $M_{Pu(NO_3)_4}$= 487.49045 g/mol.

As a result, $\boldsymbol{\rho_{solution} = 0.93989\ g/cm^3}$.

This last density solution allows, with the other calculated values and data, to determine all species concentrations in solution need for criticality calculation.

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