GENIORS

Research and Innovation Action (RIA)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 755171.

Start date : 2017-06-01 Duration : 48 Months
http://geniors.eu/

Report on the methodology to establish a density law for NCS evaluations. It will include the needs in terms of data andchemical measurements

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GENIORS - Contract Number: 755171

Project officer: Roger Garbil

Document title	Report on the methodology to establish a density law for NCS evaluations. It will include the needs in terms of data andchemical measurements
Author(s)	Mr. Marc PHILIPPE, Nicolas LECLAIRE
Number of pages	17
Document type	Deliverable
Work Package	WP9
Document number	D9.3
Issued by	IRSN
Date of completion	2019-01-31 14:21:43
Dissemination level	Public

Summary

The aim of this report is to present a methodology for establishing density laws for fissile species involved in EURO-GANEX solvents. This task part of the GENIORS Project constitutes the D9.3 deliverable (working package 9). GENIORS 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.

Approval

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2019-11-05 09:26:57	Mr. Stéphane BOURG (CEA)

RAPPORT

IRSN
INSTITUT
DE RADIOPROTECTION
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Faire avancer la sûreté nucléaire

Establishment of density laws for Nuclear Criticality Safety in the framework of the EURO-GANEX Project

GENIORS Project

N. LECLAIRE

Rapport n° PSN-EXP/SNC/2018-238

Pôle sûreté des installations et des systèmes nucléaires
Service de Neutronique et des risques de Criticité

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Rapport n° PSN-EXP/SNC/2018-238
Autres références : AF18.17

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PSN/recherche/FRM-006 01-17

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Fiche descriptive du rapport
Report description sheet

Titre

Sous-titre

Title : Establishment of density laws for Nuclear Criticality Safety in the framework of the EURO-GANEX Project

Sub title

Auteur/author(s)

Type de document : ***Document type :***	*Technical Report*	**Date de diffusion :** ***Distribution date :***	
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Mots-clés (Max. 5) :	
Key-words (Max. 5):	Density laws, EURO-GANEX, GENIORS, Solute, Solvents

RESUME

ABSTRACT

The aim of this report is to present a methodology for establishing density laws for fissile species involved in EURO-GANEX solvents. This task part of the GENIORS Project constitutes the D9.3 deliverable (working package 9). GENIORS 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.

HISTORIQUE DES MODIFICATIONS/*CHANGE HISTORY*

Indice de révision *Revision*	**Date**	**Auteur** *Author*	**Pages ou paragraphes modifiés** *Pages or paragraphs changed*	**Nature des modifications** *Nature of the changes*
A		N. LECLAIRE		

GENIORS

GEN IV integrated oxide fuels recycling strategies

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 09/10/2018

CONTENT

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1. INTRODUCTION

The GENIORS project is focused on the determination of new processes for extraction of reusable species in the framework of the reprocessing of new fuel managements. Up to now, the criticality safety assessment was performed by modelling organic solvent as water, postulating that water was conservative regarding Criticality Safety issues. The aim of the present work is to build density laws for solvents used in the new processes. The verification whether or not water is conservative when compared to new solvents will be presented in a further report.

This report is part of the D9.3 deliverable (working package 9) of the GENIORS Project. It presents a methodology for establishing density laws for fissile species involved in EURO-GANEX solvents. 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 a first part, we will describe why density laws are needed in criticality safety assessment and how these laws can be established. Then, we will focus on the strategy to establish density laws involving new solvents.

Finally, a list of measured values that are needed to build the density laws will be drawn.

2. DEFINITION OF A DENSITY LAW

Density laws link the concentration in fissile species and the moderation ratio and therefore determine the bulk density of a solution, which is rarely known. These laws are in particular used in the French criticality practice. Indeed, generally, one has only 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).

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

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Different types of density laws exist: Theoretical, Experimental and Semi empirical.

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

In fact, k_{eff} $\left(k_{eff} = \frac{\nu\Sigma_{fisson}}{\Sigma_a + Leakages}\right)$, which is the main physical parameter considered in criticality safety, is the ratio of the production of neutrons ($\nu\Sigma_{fission}$) to their absorption (Σ_a) and leakages from the system. k_{eff} value characterizes the propensity of a chain reaction to self-sustain. Then, at fixed quantity of fissile specie, the higher the density, the lower the leakages and the higher the moderation of neutrons in a solution using water as a solvent. 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, which postulate a fictitious homogenous solution of fissile media (for instance metallic uranium in solution), are used to “bound” not well characterized fissile species in a conservative approach,. 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 an existing mixture. They are based on experimental measurements and on interpolations 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 concentrations different from the ones corresponding to the measurement points.

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

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3. STRATEGY TO ELABORATE A THEORICAL DENSITY LAW

3.1. METHODOLOGY

The methodology used to build new density laws in the framework of the GENIORS project and corresponding to new solvents is the same as the one used for nitrate density laws [2]. Indeed, such laws were implemented in CRISTAL criticality safety packages [3]. It is based on PhD works defended in 2000 [4].

Such laws can be called “isopiestic” since they mix solutions with the same solvent activity. Given its experience in the field of criticality safety, IRSN has the ability to build density laws based on other solvents than water. One only needs to gather density measurements of binary mixtures (one electrolyte in the solvent).

The following paragraphs introduce different types of theoretical laws that can be used.

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.

It is always true at low concentrations (C(X) < 100-200 g/L) since low molecular interactions are observed. However, the rule is less and less followed with the solute concentration increasing. A volume contraction, due to specific interaction between the solute and the solvent, can occur and leads to higher densities than expected.

3.3. LAW BASED ON SOLVENT ACTIVITY

The solvent activity is the ratio of partial vapour pressure of the solvent between its real state and a standard state corresponding to a temperature of 25°C and a partial pressure of 1 atmosphere.

$$a_{solv} = \frac{p_{solv}}{p_{solv}^{St}} \qquad (2)$$

An alternate definition is: $a_{solv} = l_s \times x_s$

Where l_s is the activity coefficient of solvent and x_s is the mole fraction of solvent in the solution.

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3.3.1. ZDANOVSKII-STOKES-ROBINSON RULE (Z.S.R)

"When several aqueous binary solutions with the same solvent activity are mixed (isopiestic solutions), the solvent activity of the mixture obtained is identical to those of the initial solutions if there has been no chemical reaction between the salts in it" [5]. This is a limitation of the applicability of Z.S.R rule and any deviation from the law reveals the existence of chemical reactions (formation of new complexes and double salts) between the species present in the solution.

3.3.2 RYAZANOV AND VDOVENKO LAW

The mixing of binary solutions that follows the Zdanovskii rule [6] (same solvent activity) is carried out at constant volumes (volume conservation). However, for a given salt, the binary volume is not equal to its actual volume in an n-ary mixture.

3.6. ISOPIESTIC DENSITY LAW

3.6.1. DETERMINATION OF "BINARY" SOLUTIONS

For solutes presenting specific interactions with the molecules of solvent or between, the volume additive principle is not unrestrictedly followed. However, it can be applied on for specific conditions. In fact, to build a mixture of n solutes we need to split it into various "binary" solutions composed of one solute in the solvent and having the same solvent activity. As soon as we know the density of each "binary" solution, we can directly know the density of the mixture.

The first step consists in determining the various "binary" solutions and the corresponding solvent activity.

For instance, in a mixture of $UO_2(NO_3)_2$, $Pu(NO_3)_4$, nitric acid in water, three binary solutions can be constructed:

- $UO_2(NO_3)_2$ in H_2O,
- $Pu(NO_3)_4$ in H_2O,
- HNO_3 in H_2O.

The binary solutions, as well as the solvent activity, are obtained using formula (3) (Zdanovskii rule).

$$\sum_{i=1}^{n} \frac{C_i}{C_i^{bi}} = 1 \qquad (3)$$

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In fact, various C_i^{bi} values corresponding to decreasing solvent activities are tested as long as

$$\sum_{i=1}^{n} \frac{C_i}{C_i^{bi}} \neq 1.$$

Where, C_i is the molarity in the solute in the mixture and C_i^{bi} is the molarity of the solute in the binary solution that has the same solvent (H_2O) activity as the mixture.

This solvent activity is determined through a dichotomy loop on the solvent activity. Indeed, polynomial expressions give the molarity in fissile specie and the density of the corresponding "binary" solution.

3.6.2. DETERMINATION OF MIXTURE DENSITY

Once the solvent activity of the various "binary" solutions has been determined, the density of the mixture can be easily obtained through Ryazanov formula (4).

$$\rho_{mixture} = \sum_{i=1}^{n} \frac{C_i}{C_i^{bi}} \times \rho_i^{bi} = 1 \quad (4)$$

Where, ρ_i^{bi} is the density of the "binary" solution. These data can be interpolated knowing the solvent activity.

All the steps leading to the determination of the mixture density can be summarized on the flowchart given in Figure 1 [2].

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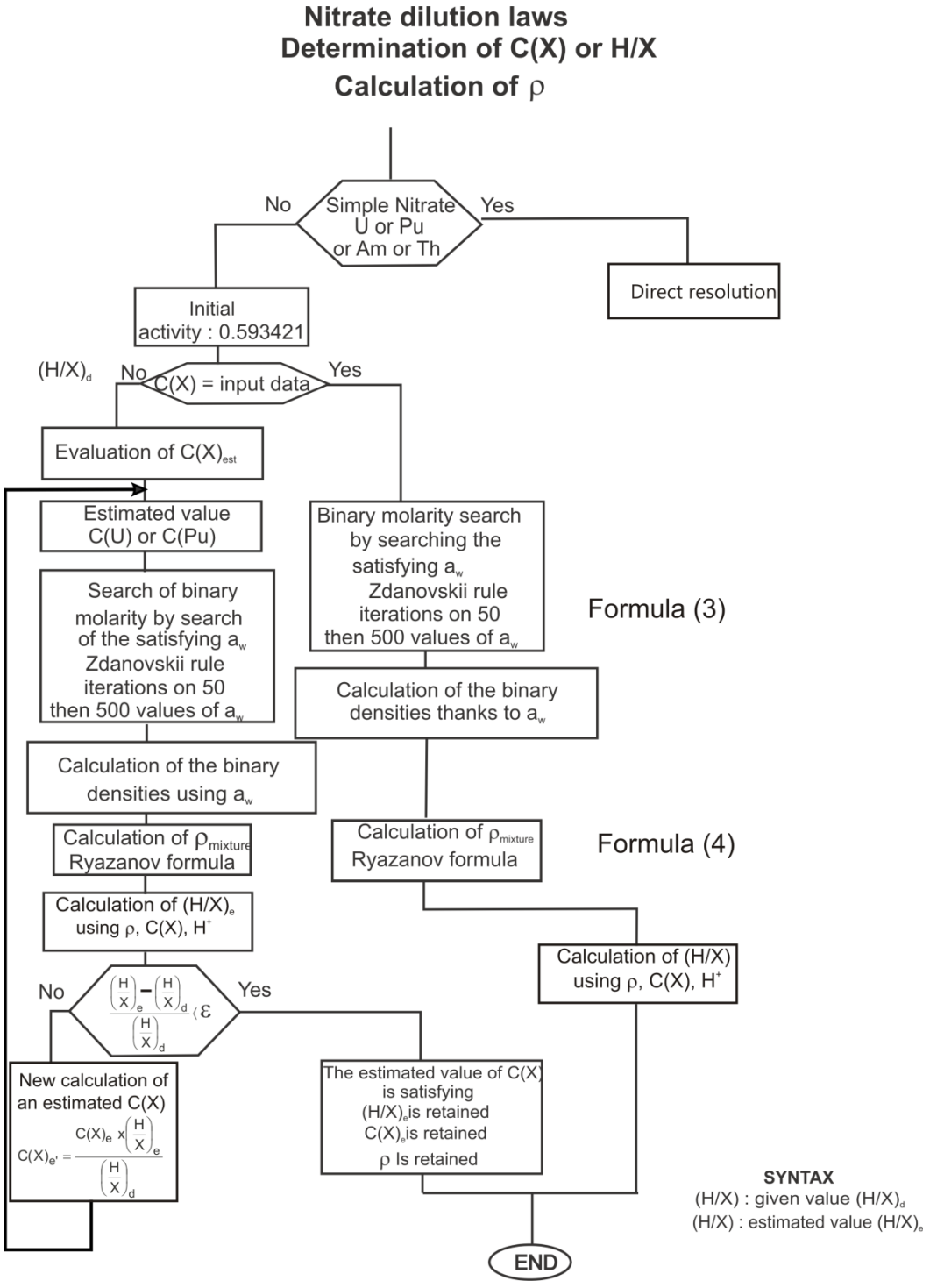

Figure 1: Flowchart of the determination of density mixture for nitrates

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4. DATA THAT ARE NEEDED

Data needed for the determination of new density laws are those necessary to define the "binary" solutions considered in the EURO-GANEX process. To define a density law, we have to collect measurement values for a wide range of solute concentrations, acidity and temperature of the process.

4.1. SOLVENT AND FISSILE SPECIES

The following data are essential regarding solvent and fissile species:

- nature and characteristics (chemical formula and their density) of the extractants and diluent adopted in the EURO-GANEX [8] process (DeHiBA and DMDOHEMA/TODGA);
- solvent ratio in the organic phase which can be hydrated and complexed and the free solvent available to complex the metal salts;
- fissile species which can be extracted and their chemical forms in aqueous and organic phases (metal, nitrate complexes/anionic, hydrolyzed or neutral forms according to the acid concentration, etc.);
- temperature at each stage of the separation process.

4.2. BULK DENSITY, SOLVENT ACTIVITY AND MOLARITY

4.2.1. MEASURED DATA

We need to know precisely the range of concentrations of the process to establish the measurement mesh. For a comparison purpose, to establish the density law of plutonium (IV) nitrate in water, 30 measurement points were performed at 25°C for:

- a concentration in plutonium varying between 0 and 640 g/l;
- water activity varying between 1 and 0.593421.

The total number of measurement points depends on the concentration range, number of electrolytes (fissile specie, nitric acid,…) and temperatures. It can therefore result in a great number of values. Thus, the delivered data will consist in tables containing the following data (see Table 1):

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Table 1: « Binary » data for a given solute (electrolyte)

Water activity (a_w)	Concentration of solute in mol/L	Density of solution in g/cm^3	Temperature (°C)
a_1	C_1	ρ_1	T_1
a_1	C_2	ρ_2	T_2
…	…	…	…
a_n	C_n	ρ_n	T_n

Data concerning saturation of the solvent and solubility limits of the solvate in the diluent are also useful to extend the density law beyond the solubility limit of the solute.

4.2.2. MEASUREMENT OF SOLVENT ACTIVITY

Before performing measurements (water activity and density) on solutions, it is required to verify if data are available for the solvents used in the EURO-GANEX process. Discussions with the partners of the GENIORS project should be conducted in order to identify the appropriate contacts.

If for some or all the solutions identified in the process, no data are available, measurements should be performed. It will be necessary to identify the device to assess solvent activities. Indeed, we know how to measure water activities. However, the question is whether or not activities of solvents other than water can be measured with the same device.

The device used to measure the water activity in reference [4] is a aw-center of Novasina company. It is composed of an electronic part and a measurement block that can easily be adapted to nuclear application. It is equipped of three cells whose description is reported on the below chart (Figure 2).

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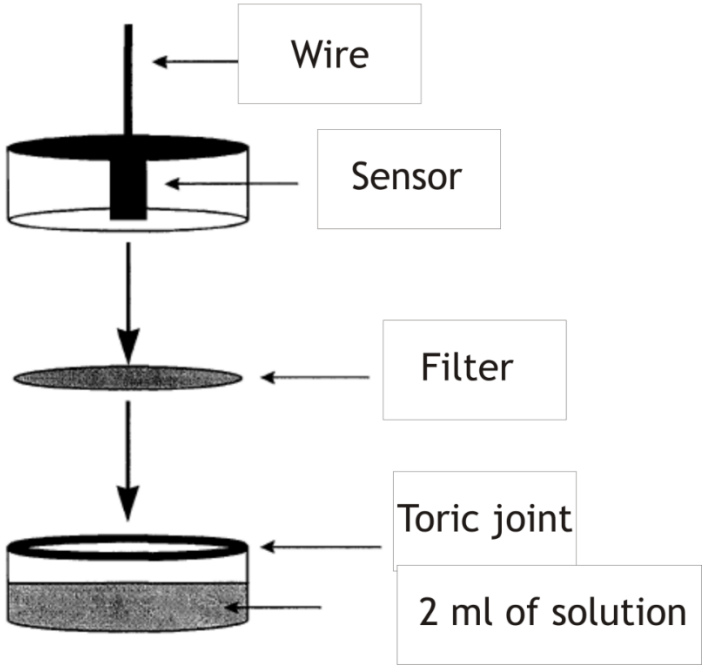

Figure 2: Measurement device of water activities.

The sensor is a solid hygroscopic electrolyte whose electrical properties vary with the water content.

A small quantity of the solution is placed between two Pt electrodes located on a glass plate. While the solution balances with ambient air, its water content takes a value which depends of the air moisture. The variations of the electric signal are measured via a high frequency signal. The response of the device is first linearized on the whole water activity range, using standard solutions saturated in electrolyte. The temperature is controlled by Peltier effect. Then a calibration is performed through lithium nitrate solutions perfectly characterized and whose water activity is known with a high level of precision.

The precision of the device on the whole range of water activity is 2% to 5%. Yet, it can be improved to better than 1% doing a calibration on a restricted range of 0.1 unit of water activity. Temperature is controlled with a precision of +/- 0.1°C on a range comprised between 15°C and 45°C.

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5. RISK ANALYSIS

Even if measurement of binary mixtures densities would not be available in the literature, delivered by the project participants or could not be performed, the comparison of the impact on k_{eff} value between the extracting solvents and water could however be roughly evaluated. The approach would consist of building a volume additive law with the extracting solvent and the various solutes (actinides, lanthanides, uranium, plutonium…). This approach requires knowing the chemical formula of the solvents and their bulk densities. Such density laws would be adequate for not too high solute concentrations.

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6. REFERENCES

[1] GENIORS European commission Directorate-general research & innovation Grant agreement Number — 755171 — GENIORS, Grant agreement number: 755171 — GENIORS — nfrp-2016-2017/nfrp-2016-2017-1

[2] J. Anno, G. Courtois, P. Dannus, N. Leclaire, G. Poullot and V. Rouyer, "Criticality calculations using the isopiestic density law of actinide nitrates", Nuclear Technology NT 12-02129, 23 Avril 2003

[3] J-M. Gomit, I. Duhamel, Y. Richet, A. Entringer, C. Magnaud, F. Malouch, C. Carmouze, « CRISTAL V2: New Package For Criticality Calculations », NCSD2017, Carlsbad, 2017

[4] N. CHARRIN, "Contribution à la caractérisation de l'écart à l'idéalité des solutions concentrées d'électrolytes: application aux cas de nitrate de plutonium IV et d'uranium IV," C.E.A-R-5891, Commissariat à l'Energie Atomique ~2000

[5] A.B. Zdanovskii, Trudy Slyanoï lab. Akad. Nauv. SSSR, 49, 237, 1953

[6] R. H. STOKES and R. A. ROBINSON, "Interactions in Aqueous Nonelectrolyte Solutions. I. Solute-Solvent Equilibria," J. Phys. Chem., 70, 2126 ~1966

[7] V. M. VDOVENKO and M. A. RYAZANOV, "Coefficients d'activité dans les systèmes à plusieurs composants," Radiokhimiya, 7, 4, 442 ~1965

[8] Robin Taylor, Mike Carrott, Hitos Galan, Andreas Geist, Xavier Hères, Chris Maher, Chris Mason, Rikard Malmbeck, Manuel Miguirditchian, Guiseppe Modolo, Chris Rhodes, Mark Sarsfield, Andreas Wilden, "The EURO-GANEX Process: Current Status of Flowsheet Development and Process Safety Studies", National Nuclear Labo Procedia Chemistry, Volume 21, 2016, Pages 524-529

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