



(51) International Patent Classification:

COIF 17/235 (2020.01) C01G 43/01 (2006.01)

(21) International Application Number:

PCT/IB2020/05546 1

(22) International Filing Date:

10 June 2020 (10.06.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

P20190101580 10 June 2019 (10.06.2019) AR

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(H))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(54) Title: METHOD FOR OBTAINING NANOPARTICULATED ASHES OF ACTINIDE, LANTHANIDE, METAL AND NON-METAL OXIDES FROM A NITRATE SOLUTION OR FROM A NITRATE, OXIDE, METAL AND NON-METAL SUSPENSION

(57) Abstract: A method for obtaining nanoparticulated ashes of oxides of actinides and lanthanides, metals and non-metals, comprising the steps of: i) preparing a nitric solution or suspension of nitrates and oxides of actinides and lanthanides, metals and non-metals, ii) adding to said nitric solution or suspension of step i) at least one monomer or polymer with acrylonitrile (C₃H₃N) functional groups; and iii) thermally treating the nitric solution or suspension of step ii) in an air atmosphere at a temperature between 185°C and 225°C to obtain nanoparticles of actinide and lanthanide oxides. Additionally, the invention provides a method for obtaining monoliths comprising adding to the nitric solution or suspension of actinides and lanthanides, metals and non-metals of step i), a glass, glass-ceramic or ceramic matrix in the form of a powder with a particle size in the range of 1-100 pm, ii) adding to said nitric solution or suspension of step i) at least one monomer or polymer with acrylonitrile (C₃H₃N) functional groups, iii) thermal treating the nitric solution or suspension from step ii) in an air atmosphere at a temperature between 185°C and 225°C to obtain nanoparticles of actinide and lanthanide oxides, iv) sintering at temperatures in the range of 610-825°C or melting at temperatures in the range of 1100-1300°C the mixture resulting from step iii) in an air atmosphere at atmospheric pressure, and in case of sintering, v) uniaxially compacting at room temperature to form a monolith.

METHOD FOR OBTAINING NANOPARTICULATED ASHES OF ACTINIDE,
LANTHANIDE, METAL AND NON-METAL OXIDES FROM A NITRATE
SOLUTION OR FROM A NITRATE, OXIDE, METAL AND NON-METAL
SUSPENSION

TECHNICAL FIELD OF THE INVENTION

The present invention relates to methods for preparing single or mixed oxides of actinides and/or lanthanides for manufacturing nuclear fuels and for preparing actinide, lanthanide, metal and non-metal oxides with the optional addition of glass, glass-ceramic or ceramic materials for conditioning and immobilization of radioactive wastes from spent fuel reprocessing.

BACKGROUND OF THE INVENTION

Denitrification is a chemical process by which a nitric acid aqueous solution containing dissolved nitrates or dissolved or suspended oxides, metals and/or non-metals, releases the nitrate group in the form of a NO_x gas, resulting in a solid product.

Generally, this kind of denitrification processes are used in order to obtain actinide oxides from nitrates so as to prepare nuclear fuel pellets as well as to treat radioactive waste streams from spent fuel reprocessing.

One of the most common denitrification methods used in this technical area consists in a nitric solution drying step followed by a thermal decomposition process at temperatures higher than 500°C for several hours [1, 2].

The drying step can be carried out in an oven, by means of microwaves, by freeze-drying, etc. Thermal treatment is usually carried out in muffles, rotary ovens, microwave ovens [3, 4], by pyrolysis [5] or flame [6], in sealed containers [7], etc. These thermal treatments produce the partial volatilization of radioactive species with low vapor pressure, such as technetium and ruthenium, among others. Moreover, when uranium is denitrified from uranyl nitrate, it is converted to the U₃O₈ phase or to the UO₃ phase, which must be transformed to the UO₂ phase (required to manufacture fuel pellets) by means of a subsequent reduction treatment [2].

Other denitrification processes used to prepare nuclear fuels use of a fluidized bed [8-10]. For example, a UO_3 fluidized bed at 270°C , where the uranyl nitrate is denitrified to UO_3 by nucleating on the bed particles. This UO_3 is then converted to UO_2 through fluorination and subsequent reduction.

Alternatively, partial chemical denitrifications with formaldehyde, formic acid and sugar at about 100°C , followed by calcination at over 400°C to decompose residual nitrates, have been implemented to treat high-level wastes on a laboratory and industrial scale since the early 80s [11, 12].

In the method of the present invention, the process temperature does not exceed 225°C and the treatment time is less than 2 hours, which not only prevents the volatilization of radioactive species, but also reduces the cost of the operation. Moreover, this treatment does not require subsequent calcination at temperatures higher than 400°C , since the entirety of the compounds are denitrified in a single step.

Furthermore, by applying the method of the present invention to uranium, thorium, uranium-thorium mixtures, and/or mixtures of these actinides with burnable poisons such as gadolinium, samarium, europium and erbium, the desired nanoparticulated phases are obtained in a controlled manner, varying certain parameters of the process, without the need for subsequent treatments (among others: U_3O_8 , UO_2 , ThO_2 , $(\text{U,Th})\text{O}_2$, $(\text{U,Gd})\text{O}_2$, $(\text{Th,Gd})\text{O}_2$, $(\text{Th,Sm})\text{O}_2$ y $(\text{U,Th,Gd})\text{O}_2$).

In the field of manufacture of nanoparticulated fuel materials there are few published syntheses that produce uranium dioxide with particle sizes smaller than 100 nm. Among them, two main approaches can be highlighted : radiation-assisted synthesis (gamma and electrons) and wet or gaseous chemical synthesis.

Within the first group, methods called "radiation chemical synthesis" stand out. This route produces the reduction of U(VI) to U(IV), with the consequent coalescence and precipitation of uranium dioxide nanoparticles, from reducing or oxidizing agents obtained by exposing a precursor solvent to ionizing radiations. For example, 80 nm and 9 nm nanoparticles were obtained, synthesized from a uranyl nitrate solution in the presence of 2-propanol using gamma radiation from a Co-60 source or 6 MeV electrons, respectively [13].

Also, depleted UO_2 nanoparticles were obtained through gamma irradiation for at least 7 days from an acidic uranyl nitrate solution with a Co-60 source. The reported final solution still contains a mixture of nanoparticles of uranium dioxide and uranyl nitrate remaining in solution [14].

Unlike these routes, the present method used to generate UO_2 nanoparticles in this size range does not require any radioactive source, is much shorter (less than 2 hours) and has a 100% uranyl nitrate conversion efficiency (no remaining uranyl nitrate or liquid effluents). In addition, the nanoparticles are synthesized and processed in air, requiring no glove boxes, no controlled atmosphere and/or no vacuum.

Within the group of wet chemical routes, coprecipitation followed by thermal denitrification and reduction is one of the best-known methods for obtaining uranium dioxide [2]. Within this type are coprecipitation via ammonium diuranate (ADU) formation or via ammonium uranyl carbonate (AUC) formation. These routes are combinations of different physical-chemical processes involving treatments in different atmospheres and at high temperatures to finally obtain UO_2 , which is about 100 nm in size. According to the inventors' experiments, the synthesis of 100g of UO_2 by the ADU method requires about 48 hours of preparation, using an oven drying process at 100°C , an air treatment up to temperatures of 800°C for 6 to 8 hours to pass the ADU to the U_3O_8 crystalline phase, and a third thermal treatment of about 6 to 8 hours at 700°C in a reducing atmosphere to pass from U_3O_8 to UO_2 . In addition, this process generates about 2 liters of liquid ammonia residues contaminated with uranium, plus filter paper. Unlike these routes, the invention process is shorter, requires only one furnace step and does not require a special atmosphere (it is done in air).

Other wet syntheses use thermal decomposition of an organic precursor. For example, Wu et al. (2006) [15] start from a uranyl acetylacetonate solution with oleic acid, oleylamine and 1-octadecene to produce colloidal UO_2 nanoparticles of about 5 nm by thermal decomposition of the precursor at 295°C . This synthesis requires an extraction step in hexane and acetone mixtures, and subsequent filtration. In opposition, the present inventive process of denitrification and conversion to uranium oxide nanoparticles does not use organic solvents or require an extraction/filtration step, the reaction occurring at temperatures about $70\text{-}110^\circ\text{C}$ lower than that above

and without generating liquid effluents. In addition, in the present case the particles are not monodisperse, favoring the formation of a compact.

There is also a non-aqueous synthesis, partly based on the Wu's synthesis [15], in which uranium acetylacetonate is introduced into a mixture of dibenzyl-ether with oleic acid, oleylamine, trioctylamine, and trioctylphosphine, and is heated to 280°C [16]. The UO_2 nanoparticles, of about 5 nm, are then precipitated in ethanol. In this case the same considerations apply as for the Wu's synthesis [15].

Another synthesis of this type is based on the thermal decomposition of uranium oxalate. Tyrpekel et al. (2015) [17] for example, report obtaining UO_2 particles of about 10 nm from a uranyl nitrate mixture electro-reduced to U(IV) in solution of oxalic acid, nitric acid and hydrazine and treated at 600°C for one hour in argon atmosphere. Unlike this synthesis, the method of the invention does not require a previous reduction step, it is performed at a temperature about 400°C lower than that above and does not require an inert atmosphere since it takes place in air.

A variation of these organic syntheses is reported by Wang et al. (2008) [18]. In this synthesis, $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ is mixed with water and ethanoldiamine to form a solution that is processed within an autoclave for 48 hours at 160°C. The extraction requires the steps of washing in ethanol, centrifugation and drying. The nanoparticles of uranium dioxide obtained have an approximate size between 100-150 nm with a reported yield of 85%. Unlike this route, the process of the invention does not involve the use of autoclaves or washing and centrifugation processes and, in addition, the time required is lower in more than one order of magnitude.

In addition to chemical routes and radiolysis methods, biological methods for obtaining UO_2 nanoparticles have also been reported. However, these require the use of cells or bacteria, which are absent in synthesis of the present invention.

In addition, methods are known in the state of the art which allow the conversion of lanthanides into oxides of such elements incorporating polymers. For example, the Russian patent RU 2008147496 (A) is known to disclose a process for the preparation of lanthanide oxide powders, which comprises precipitating a lanthanide salt from nitric acid solutions, separating, washing, drying, and heat treating the same to produce

lanthanide oxides. The salt precipitation is carried out from nitrate solutions of the lanthanide and a concentration of 30-50 g/L for the oxalic acid with the continuous introduction of polyacrylamide ($C_3H_3ONH_2$ groups) in the form of a solution with a concentration of 0.005-0.015% in an amount of 5.0-10.0 mg per 1.0 kg of lanthanide oxide, while the oxalate is precipitated as a lanthanide salt, the thermal treatment is carried out for 2.0-2.2 hours in the temperature range of 380-825°C, depending on the properties of the individual lanthanides.

Drying is carried out at 60-65°C to a residual moisture content of 5-6%.

In said process several steps are required where salts precipitate and temperature ranges are higher than those used by the present invention, making such methods complex and expensive to implement. On the contrary, the present invention introduces notable advantages with respect to this background known to the inventors:

In the method of the present invention, total thermochemical denitrification at low temperature in air and at atmospheric pressure makes it possible to obtain in a single step nanoparticulated ashes from a solution or suspension of nitrates, actinide and/or lanthanide oxides, metals and non-metals in nitric acid, adding at least one monomer or polymer with acrylonitrile (C_3H_3N) functional groups, achieving total thermochemical denitrification in air atmosphere, at atmospheric pressure and at a temperature between 185°C and 225°C -depending on the composition of the nitrate solution or suspension of nitrates, oxides, metals and non-metals to be denitrified- for short periods of time between 11 and 114 minutes, by means of a thermal treatment at a constant heating rate (between 1.8 and 10°C/min) and without the need for subsequent thermal treatment at a constant temperature (calcination).

The method of the present invention does not require the use of radioactive sources, nor prior or subsequent reduction steps, nor subsequent thermal treatments at a constant temperature (calcinations). Furthermore, it does not generate liquid or solid effluents, it does not involve salt precipitation stages, nor solid separation stages -such as filtering or centrifugation- nor washing, drying, or subsequent calcinations, and results in dry and homogeneous nanoparticulated ashes, in which most of the elements are in the required crystalline phase of their oxides. Another advantage of the

present invention lies in the total conversion time of nitrates to oxides due to the absence of a calcination stage.

In the prior art, on the contrary, a calcination stage is included, which adds the times required to achieve the heating ramp and the cooling ramp of the calcination process as well as the precipitation times in the case of salt formation, the separation times of such salts by filtration, the washing and drying times of such salts to finally convert them into oxides by calcination. Additionally, the present invention utilizes a process temperature not exceeding 225°C, which not only avoids the volatilization of radioactive species, but also reduces the cost of operation since it does not require thermal treatments at constant temperature (calcinations) at any temperature above 225°C.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows the X-ray diffractogram (a) and electron diffractogram (b) of a simulated waste sample. TEM micrographs in clear field (c) and high resolution (d).

Figure 2: SEM micrographs of a waste sample (a). Area where the mapping was performed with EDS (b) and EDS spectrum of the waste sample (c).

Figure 3: X-ray diffractogram (a) and electron diffractogram (b) of a simulated waste sample with glass aggregate. TEM micrographs in dear-field (c) and high resolution (d).

Figure 4: SEM micrographs of the ash and glass sample (a). Area where EDS mapping was performed (b) and EDS spectrum of the sample (c).

DETAILED DESCRIPTION OF THE INVENTION

Therefore, the present invention provides a method for obtaining nanoparticulated ashes from oxides of actinides and lanthanides, metals and non-metals, comprising the steps of:

- i) preparing a nitric solution or suspension of nitrates and oxides of actinides and lanthanides, metals and non-metals,
- ii) adding to such nitric solution or suspension of step i) at least one monomer or polymer with acrylonitrile (C_3H_3N) functional groups; and

iii) thermally treating the nitric solution or suspension from step ii) in air atmosphere at a temperature of between 185°C and 225°C to obtain nanoparticles of actinide and lanthanide oxides.

In a preferred embodiment of the invention the thermal treatment is carried out at a constant heating rate starting from room temperature (20°C) or at 75°C, reaching 225°C in less than 2 hours with the heating ramp being 1.8-10°C/min.

Preferably, the monomer or polymer with acrylonitrile (C_3H_3N) functional groups has a molecular weight of the repetition unit between 53.06 g/mol and 150000 g/mol for a typical polymer chain and has between 2000 and 5000 acrylonitrile groups, preferably approximately 3000 acrylonitrile groups.

In a more preferred embodiment of the invention, the polymer is polyacrylonitrile.

The concentrations or precursor of individual actinides, mixtures of actinides, lanthanides and actinide/lanthanide mixtures (expressed as oxides) in the nitrate solution are between 250 and 500 g/L.

The invention also provides a method for obtaining monoliths employing the method described above comprising the addition to the nitric solution or suspension of nitrates and oxides of actinides and lanthanides, metals and non-metals of step i) a glass, glass-ceramic or ceramic matrix in the form of a powder with a particle size range of 1-100 pm,

ii) adding to said nitric solution or suspension of step i) at least one monomer or polymer with acrylonitrile (C_3H_3N) functional groups,

iii) thermal treating the nitric solution or suspension from step ii) in air atmosphere at a temperature between 185°C and 225°C to obtain nanoparticles of actinide and lanthanide oxides,

iv) sintering at temperatures in the range of 610-825°C or melting at temperatures in the range of 1100-1300°C the mixture resulting from step iii) in air atmosphere at atmospheric pressure, and, in case of sintering,

(v) compacting uniaxially at room temperature to form a monolith.

Preferably, the glass matrix is alumino-borosilicate glass powder in mass ratio of oxides in the range 1:1 to 9:1.

In step i) the concentrations of precursors of individual actinides, actinide mixtures, lanthanides and actinide/lanthanide mixtures (expressed as oxides) in the nitrate solution is between 250 and 500 g/L.

In another preferred embodiment of the invention for obtaining fuel tablets or pellets with burnable poisons, the method comprises adding oxides or nitrates of neutron poisons selected from gadolinium, samarium and erbium, to the solution or nitric dispersion of step i) comprising a glass matrix.

With the methods of the present invention it is possible to obtain particulate or monolithic combustible materials such as fuel tablets or pellets from nitrates and oxides of actinides and lanthanides, metals and non-metals selected from nitrates and oxides of Rb, Mr, Y, Ag, Cd, Cs, Ba, Ce, U, Fe, Zr, Ni, Sn, La, Pr, Nd, Sm, Eu, Gd, Cr, P, Se, U, Te, Rh, Ru, Mo, Th, uranium-thorium mixtures, and/or mixtures of these actinides with burnable poisons such as gadolinium, samarium, europium, and erbium.

The method of the present invention has numerous advantages among which it is noticeable that it does not generate liquid or solid effluents, and it results in a nanoparticulated and homogeneous ash, in which most of the elements are in the crystalline phase of their oxides.

The method of the present invention is completed during heat treatment at constant heating rate (heating ramp of 1.8-10°C/min), starting from room temperature (20°C) or at 75°C, reaching up to 225°C in less than 2 hours, and it does not require heat treatment (calcination) at any temperature above 225°C, since all nitrates are decomposed and converted in a controlled way to oxides in a single step, during the heating ramp.

The method of the present invention allows the direct and controlled conversion of nitrates to oxides with the required crystalline phases.

Indeed, actinides, lanthanides, metals and non-metals dissolved or suspended in nitric acid are directly converted to oxides with no remnants of nitrogen or carbon from monomers or polymers with acrylonitrile (C_3H_3N) functional groups which are decomposed and removed as nitrogen and carbon oxides, and without the need for conversion to a salt.

In the case of elements such as uranium, which form more than one stable oxides at room temperature, the used amount of monomer or polymer with acrylonitrile (C_3H_3N) functional groups makes it possible to control which oxides and in what proportions they are to be obtained. By applying the method of the present invention to uranium, thorium, uranium-thorium mixtures and/or mixtures of uranium with burnable poisons such as gadolinium, samarium, europium and erbium, the different individual oxides or solid solutions of the mixed oxides with the required nanoparticulated crystalline phases, among others, UO_2 , U_3O_8 , $(U,Gd)O_2$, $(U,Gd)_3O_8$, $(U,Th)O_2$ and $(U,Th,Gd)O_2$, are obtained in a controlled manner.

An additional advantage is the high efficiency of conversion of nitrates to oxides. According to the method of the present invention, a conversion efficiency of 100% of the nitrates of actinides, lanthanides and their mixtures is achieved for any initial concentration of same, without remnants of nitrates, monomers or polymers with acrylonitrile (C_3H_3N) functional groups, or liquid effluents. Furthermore, the nanoparticles obtained by the method of the present invention are synthesized and processed in air, requiring no glove box, controlled atmosphere and/or vacuum.

The method of the present invention does not use organic solvents and/or reagents, apart from the monomer or polymer with acrylonitrile (C_3H_3N) functional groups, nor does it generate wastes and/or liquid effluents.

Another important advantage is the absence of intermediate steps: in the present method of total thermochemical denitrification at low temperature and simultaneous and controlled conversion to a nanoparticulated ash, it does not require other intermediate steps commonly present in published methods such as autoclave treatments or extraction in another organic phase.

For these reasons, the method of the present invention is highly effective since it has the ability to achieve the conversion of nitrates to oxides in a shorter time with less energy consumption because it takes place in a single step, and it is carried out at a lower temperature than in the processes of the prior art.

Moreover, the method of the present invention entails lower economic costs, since it starts from higher concentrations - between 250 and 500 g/L (expressed as oxides) in the nitrate solution, unlike the Russian patent

application RU 2008/147496 in which the nitrate solution can have lanthanide concentrations (expressed as oxides) of 30-50 g/L. Also, the method of the present invention does not generate liquid or solid wastes and has a 100% efficiency regardless of the initial concentration of actinides, lanthanides or their mixtures in the nitric acid solution.

According to another significant advantage, in the case of processing radioactive materials, the absence of additional steps minimizes the exposure of the staff to ionizing radiations and the requirements for laboratory material, devices and equipment, the decontamination of which generates secondary liquid and solid waste streams that must be managed safely in accordance with the standards set forth by the Nuclear Regulatory Authority (RNA).

Introduction and function of the monomer or polymer:

The use of polymers to promote the production of actinide and lanthanide oxides has been described in the prior art. However, as taught by the patent application RU 2008/147496 described in the background section of the invention, the continuous introduction of a solution of the polymer - polyacrylamide- during the precipitation from the nitric solution has the function of accelerating the precipitation and preventing the agglomeration of the oxalate, which, after additional steps of separation by filtration, washing and drying, is finally converted to oxide by calcination. Unlike this disclosure, in the method of the present invention the introduction of at least one monomer or polymer with acrylonitrile (C_3H_3N) functional groups into the initial nitric solution has the function of totally denitrifying and converting the nitrates to oxides in a controlled manner in a single step.

Obtaining individual oxides of lanthanides, actinides, metals and non-metals and their mixtures:

The method of the present invention makes it possible to obtain a dry nanoparticulated ash from individual lanthanide oxides as well as from solid solutions of mixed oxides of two or more lanthanides, solid solutions of mixed lanthanide and actinides oxides, individual actinide oxides, solid solutions of mixed actinide oxides, oxides of one or more metals, oxides of one or more non-metals, and any mixture of the aforementioned.

The most significant difference is the use of monomer or polymer with acrylonitrile (C_3H_3N) functional groups which results in an inventive step of total denitrification, controlled conversion of nitrates to oxides and total removal of the organic compound as gaseous nitrogen and carbon oxides in a single step. For that reason, the use of at least one monomer or polymer with acrylonitrile (C_3H_3N) functional groups has a critical function in the process of the present invention. Indeed, among the advantages of using materials with acrylonitrile groups the following can be mentioned:

- a) In the case of elements such as uranium, which have more than one stable oxide at room temperature, the amount of monomer or polymer with acrylonitrile (C_3H_3N) functional groups that is used allows for controlling which oxides and in which proportions they are to be obtained. For example, for uranium, thorium, uranium-thorium mixtures and/or mixtures of uranium with burnable poisons such as gadolinium, samarium, europium and erbium, the different individual oxides or solid solutions of the mixed oxides with the required nanoparticulated crystalline phases, among others, UO_2 , U_3O_8 , $(U,Gd)O_2$, $(U,Gd)_3O_8$, $(U,Th)O_2$ and $(U,Th,Gd)O_2$, are obtained in a controlled way.
- b) The use of monomer or polymer with acrylonitrile (C_3H_3N) functional groups (molecular weight of the repetition unit between 53.06 g/mol and 150000 g/mol for a typical polymer chain with approximately from 2000 to 5000 acrylonitrile groups, preferably 3000 acrylonitrile groups) allows for higher reaction yields to be obtained by using concentrations of individual actinides, actinide mixtures, lanthanides and actinide/lanthanide mixtures (expressed as oxides) between 250 and 500 g/L in the nitrate solution.
- c) The direct and controlled conversion of nitrates to oxides using monomer or polymer with acrylonitrile (C_3H_3N) functional groups is applied to individual actinides or their mixtures, individual lanthanides or their mixtures, mixtures of actinides with lanthanides, mixtures of actinides, lanthanides, metals and non-metals.
- d) Since salt precipitation from nitrates does not occur, but rather the direct and controlled conversion of nitrates to oxides through the use of monomer or polymer with acrylonitrile (C_3H_3N) functional groups, the use of additional reagents is avoided and steps such as salt precipitation, filtration, washing, drying and calcination are eliminated.

e) The direct and controlled conversion of nitrates to oxides by the use of monomer or polymer with acrylonitrile (C_3H_3N) functional groups involves a single step -which takes place during thermal treatment at a constant rate up to a temperature of $225^{\circ}C$ and in less than 2 hours without producing liquid or solid effluents- when compared to the method of the prior art using polyacrylamide, results in a lower energy consumption, lower input cost in inputs, devices and equipment and no generation of secondary solid or liquid waste streams as occurs in processes where there is salt precipitation.

The method of the present invention is useful in the following applications:

- For the treatment of high level waste streams containing actinides, lanthanides, metals and non-metals (fission, activation and corrosion products from the reprocessing of spent fuel) a glass, glass-ceramic or ceramic matrix is added in the form of a fine powder (with a particle size range of 1-100 μm) to the nitric solution and then the latter is denitrified by following the described process. The resulting mixture may be melted and/or sintered in the case of glass at temperatures in the range of $1100-1300^{\circ}C$ or $610-825^{\circ}C$ respectively, in air atmosphere at atmospheric pressure and, in the case of sintering, the mixture must be compacted uniaxially at room temperature under pressures in the range of 24-132 MPa), forming a highly homogeneous decomposition monolith with reduced volume, which immobilizes the waste. The great advantage of this denitrification and matrix incorporation method is that it occurs at low temperatures, preventing the volatilization of radioactive compounds.
- To prepare fuel tablets or pellets from oxides and/or mixed oxides, the nanoparticulated ash with a size range from 5 to 100 nm obtained from denitrification of actinide oxides or nitrates by this process, is granulated by uniaxial pre-compaction without the use of additives and by extrusion through a sieve mesh with a 2 mm opening without the use of additives, and is processed according to the conventional industrial method by uniaxially compaction at room temperature and sintering in an inert atmosphere (helium, argon and nitrogen, among others) or reducing atmosphere (hydrogen, and mixtures of hydrogen with the aforementioned inert gases, among others).
- To prepare fuel tablets or pellets with burnable poisons, oxide nitrates of neutron poisons (gadolinium, samarium and erbium, among others) are

added to the nitric solution and the same procedure described in the previous paragraph is followed.

- To prepare fuel tablets or pellets of oxides and/or mixed oxides when the necessary infrastructure to handle transuranic elements is not available, the nanoparticulated ash (with a size range from 5 to 100 nm) obtained from the denitrification of oxides or nitrates of thorium and/or uranium and cerium, is granulated by uniaxial pre-compaction without the use of additives and by extrusion through sieve mesh with a 2 mm opening, and is processed according to the conventional industrial method, by uniaxially compaction at room temperature and sintering in an inert atmosphere (helium, argon, nitrogen, among others) or reducing atmosphere (hydrogen and mixtures of hydrogen with the aforementioned inert gases, among others).

The obtained tablets or pellets can be used in the fuel elements of power reactors currently in commercial operation (3 in Argentina, 442 worldwide). In addition, the granulated material can be shaped into the appropriate geometry for the manufacture of fuel elements for propulsion nuclear reactors (ships, submarines, etc.), for research reactors, etc.

- To prepare tablets or pellets to simulate nuclear fuels when the necessary infrastructure to handle radioactive material is not available, the nanoparticulated ash with a size range from 5 to 100 nm obtained from the denitrification of cerium oxides or nitrates, with or without the addition of oxides or nitrates of burnable poisons, is granulated by uniaxial pre-compaction without the use of additives and by extrusion through a sieve mesh with a 2 mm opening without the use of additives and processed according to the conventional industrial method by uniaxial compaction at room temperature and sintering in an inert atmosphere (helium, argon and nitrogen, among others) or reducing atmosphere (hydrogen, and mixtures of hydrogen with the aforementioned inert gases, among others).

- To prepare nanoparticulated catalysts with high specific area of metals and/or lanthanides.

Experimental section

- a. Weighing the required quantities of the precursors (between 250 and 500 g/L expressed as actinide, lanthanides, metals and/or non-metals) oxides and
- b. Suspending or solubilizing in nitric acid analytical grade,
- c. Shaking the suspension at a constant speed, between room temperature and 75°C.
- d. Adding between 0.4 and 4% by weight of polyacrylonitrile of any length with acrylonitrile (C_3H_3N) functional groups with molecular weight of the repetition unit 53.06 g/mol (Aldrich, Hisisa or other).
- e. Shaking until a homogeneous suspension is achieved.
- f. Carrying out a thermal treatment at a constant heating rate of 1.8 - 10°C/min, up to 185-225°C, in air atmosphere,
- g. Removing from oven, cooling in air until reaching room temperature

Immobilization process

If it is desired to immobilize radioactive wastes, a glass, glass-ceramic or ceramic matrix is added in the form of a fine powder (with a particle size range of 1-100 pm) to the nitric solution during step b). After step g) the material is thermally treated (step h)) at the temperature required for melting (at temperatures in the range of 1100-1300°C) or sintering (at temperatures in the range of 610-825°C).

Sinterable Monolith

If a monolith that can be sintered is desired, the material obtained in step h) or g) is compacted according to any conventional method and is subjected to a thermal treatment. In the case that the sintered monoliths are nuclear fuel tablets or pellets of oxides and/or mixed oxides with or without burnable poison, the material obtained in step h) is granulated by uniaxial pre-compaction without the use of additives and by extrusion through a sieve mesh with a 2 mm opening and is processed according to the conventional industrial method by uniaxially compaction at room temperature (under compaction pressures in the range of 200-600MPa) and sintering at atmospheric pressure in an inert atmosphere (helium, argon and nitrogen, among others) or reducing atmosphere (hydrogen, and mixtures of hydrogen with the aforementioned inert gases, among others)

at temperatures in the range of 1700-1800°C. In the event that the sintered monoliths are the result of the radioactive waste immobilization process, the material obtained in g) is processed according to the conventional industrial method by uniaxially compaction at ambient temperature (under compaction pressures in the range of 20-200 MPa) and sintering at atmospheric pressure in air atmosphere at temperatures in the range of 500-850°C.

Radioactive Waste Treatment:

Assay 1: Denitrification of simulated high-level liquid radioactive wastes.

Assay 2: Denitrification of simulated high-level liquid radioactive wastes and incorporation into a glass matrix.

Preparation of Nuclear Fuel Materials:

Assay 3: Denitrification of uranium nitrate/oxide and controlled conversion to obtain nanoparticulated uranium oxides (UO_2/U_3O_8) (nuclear fuel).

Assay 4: Denitrification of uranium nitrate/oxide and gadolinium nitrate/oxide to obtain a solid solution of nanoparticulated $(U,Gd)O_2$ (nuclear fuel with burnable poison).

Assay 5: Denitrification of uranium nitrate/oxide and thorium nitrate/oxide to obtain a solid solution of nanoparticulated $(U,Th)O_2$ (mixed nuclear fuel).

Assay 6: Denitrification of uranium nitrate/oxide and cerium nitrate/oxide to obtain a solid solution of nanoparticulated $(U,Ce)O_2$ (mixed simulated nuclear fuel).

Assay 7: Denitrification of cerium nitrate/oxide and gadolinium nitrate/oxide to obtain a solid solution of nanoparticulated $(Ce,Gd)O_2$ (simulated nuclear fuel with burnable poison).

Other Applications:

Assay 8: Denitrification of cerium nitrate/oxide and zirconium nitrate/oxide to obtain a solid solution of nanoparticulated $(Ce,Zr)O_2$ (Catalyst).

Waste treatment:

Assay 1: Denitrification of simulated high-level liquid wastes:

A suspension in 3 molar HNO_3 is prepared with nitrates (Rb, Sr, Y, Ag, Cd, Cs, Ba, Ce, U, Fe), oxides (Zr, Ni, Sn, La, Pr, Nd, Sm, Eu, Gd, Cr, P, Se, U), and metals (Te, Rh, Ru, Mo) in the proportions indicated in Bevilacqua 1992 [19] corresponding to the reprocessing of spent fuel from nuclear power reactors. To a 10 ml aliquot of this suspension at 60°C under constant agitation, 0.4-4% by weight of polyacrylonitrile (Aldrich or Hisisa) is added. Thermal treatment is carried out at a constant heating rate of 1.8-10°C/min up to a temperature in the range of 185-225°C. The ash obtained was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). These microscopes have a detector that allows for the chemical composition to be known through the energy dispersive spectroscopy (EDS) technique.

It was also possible to perform an electron diffraction with the TEM.

Figure 1 shows the X-ray diffractogram (a) and electron diffractogram (b) of a simulated residue waste sample. TEM micrographs in clear field (c) and high resolution (d).

In Figure 2, the results of the observation of the samples in the scanning electron microscope (SEM) can be seen. In this equipment it was possible to perform an analysis of the microstructure and then an area was selected to make an EDS scan. In the table with the results of the chemical composition of the ashes (c), a high content of carbon is seen (45.4%), which corresponds to the tape on which the sample is supported.

Assay 2: Denitrification of simulated high-level liquid wastes and incorporation into a glass matrix:

The suspension is prepared as in Assay 1 and powdered aluminoborosilicate glass is added in a mass ratio of oxides in the range 1:1 to 9:1. To a 10 ml aliquot of this suspension at 60°C under constant agitation, 0.4-4% by weight of polyacrylonitrile is added (Aldrich or Hisisa). A thermal treatment is carried out at a constant heating rate of 1.8-10°C/min up to a temperature in the range of 185-225°C. The ash obtained was studied by XRD, TEM, SEM-EDS.

Figure 3 shows the X-ray diffractogram (a) and electron diffractogram (b) of a simulated glass aggregated waste sample. Clear-field (c) and high resolution (d) TEM micrographs studied by XRD, TEM, SEM-EDS.

Figure 4 shows SEM micrographs of the ash and glass sample (a). Area where EDS mapping (b) and EDS spectrum of the sample (c) were performed.

Preparation of Nuclear Fuel Materials:

Assay 3: Denitrification and controlled conversion to obtain nanoparticulated uranium oxides (UO_2 / U_3O_8) (nuclear fuel):

A 1 molar solution of uranyl nitrate or uranium oxide in nitric acid is prepared. To an aliquot of 10 ml, 0.4-4% by weight of polyacrylonitrile (Hisisa) is added. A thermal treatment is carried out at a constant heating rate between 1.8-10°C/min to a temperature in the range of 185-225°C. The obtained compound was studied by XRD and TEM techniques, by means of which it was determined that the compound presents the desired phase (UO_2 or U_3O_8 , as appropriate) and the particle size is less than 10 nm.

Assay 4: Denitrification to obtain a solid solution of nanoparticulated $(\text{U,Gd})\text{O}_2$ (Nuclear fuel with burnable poison):

A 1 molar solution of uranium nitrate or oxide is prepared with 10% by weight of nitrate or gadolinium oxide in nitric acid. To an aliquot of 10 ml, 0.4-4% by weight of polyacrylonitrile is added (Hisisa). A thermal treatment is carried out at a constant heating rate of 1.8-10°C/min up to a temperature in the range of 185-225°C. The obtained compound was studied by XRD and TEM techniques, by means of which it was determined that the compound presents the desired phase (UO_2 with gadolinium incorporated in the structure) and the particle size is less than 10 nm.

Assay 5: Denitrification to obtain a solid solution of nanoparticulated $(\text{U,Th})\text{O}_2$ (Mixed nuclear fuel):

A 1 molar solution of uranium nitrate or oxide is prepared with 10% by weight of thorium nitrate or oxide in nitric acid. To an aliquot of 10 ml, 0.4-4% by weight of polyacrylonitrile (Hisisa) is added. A thermal treatment is carried out at a constant heating rate of 1.8-10°C/min up to a temperature in the range of 185-225°C. The obtained compound was studied by XRD and TEM techniques, by means of which it was determined that the

compound presents the desired phase (UO_2 with thorium incorporated in the structure) and the particle size is less than 10 nm.

Assay 6: Denitrification to obtain a solid solution of nanoparticulated $(\text{U,Ce})\text{O}_2$ (Mixed simulated nuclear fuel):

A 1 molar solution of uranium nitrate or oxide is prepared with 10% by weight of cerium nitrate/ oxide in nitric acid. To an aliquot of 10 ml, 0.4-4% by weight of polyacrylonitrile is added (Hisisa). A thermal treatment is carried out at a constant heating rate of $1.8\text{-}10^\circ\text{C}/\text{min}$ up to a temperature in the range of $185\text{-}225^\circ\text{C}$. The obtained compound was studied by XRD and TEM techniques, by means of which it was determined that the compound presents the desired phase (UO_2 with cerium incorporated in the structure) and the particle size is less than 10 nm.

Assay 7: Denitrification to obtain a solid solution of nanoparticulated $(\text{Ce,Gd})\text{O}_2$ (Simulated nuclear fuel with burnable poison):

A 1 molar solution of cerium nitrate or oxide is prepared with 10% of gadolinium nitrate or oxide in nitric acid. To an aliquot of 10 ml, 0.4-4% by weight of polyacrylonitrile is added (Hisisa). A thermal treatment is carried out at a constant heating rate of $1.8\text{-}10^\circ\text{C}/\text{min}$ up to a temperature in the range of $185\text{-}225^\circ\text{C}$. The obtained compound was studied by XRD and TEM techniques, by means of which it was determined that the compound presents the desired phase (CeO_2 with gadolinium incorporated in the structure) and the particle size is less than 10 nm.

Other Applications:

Assay 8: Denitrification to obtain a solid solution of nanoparticulated $(\text{Ce,Zr})\text{O}_2$ (Catalyst):

A 1 molar solution cerium of nitrate/ oxide is prepared with 20% by weight of zirconium nitrate or oxide in nitric acid. To an aliquot of 10 ml, 0.4-4% by weight of polyacrylonitrile is added (Hisisa). A thermal treatment is carried out at a constant heating rate of $1.8\text{-}10^\circ\text{C}/\text{min}$ up to a temperature in the range of $185\text{-}225^\circ\text{C}$. The obtained compound was studied by XRD and TEM techniques, by means of which it was determined that the

compound presents the desired phase (CeO_2 with zirconium incorporated in the structure) and the particle size is less than 10 nm.

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CLAIMS

1. A method for obtaining nanoparticulated ashes of oxides of actinides and lanthanides, metals and non-metals, comprising the steps of:
 - i) preparing a nitric solution or suspension of nitrates and oxides of actinides and lanthanides, metals and non-metals,
 - ii) adding to said nitric solution or suspension of step i) at least one monomer or polymer with acrylonitrile (C_3H_3N) functional groups; and
 - iii) thermally treating the nitric solution or suspension of step ii) in an air atmosphere at a temperature between $185^{\circ}C$ and $225^{\circ}C$ to obtain nanoparticles of actinide and lanthanide oxides.
2. The method according to claim 1, wherein the thermal treatment is carried out at a constant heating rate starting from room temperature ($20^{\circ}C$) or up to $75^{\circ}C$, reaching $225^{\circ}C$ in less than 2 hours.
3. The method according to claim 2, wherein the thermal treatment is carried out at a heating ramp of $1.8-10^{\circ}C/min$.
4. The method according to claim 1, wherein the monomer or polymer with acrylonitrile (C_3H_3N) functional groups has a molecular weight of the repeating unit between 53.06 g/mol and 150000 g/mol for a typical polymer chain and has between 2000 and 5000 acrylonitrile groups, preferably about 3000 acrylonitrile groups.
5. The method according to claim 4, wherein the polymer is polyacrylonitrile.
6. The method according to claim 1, wherein the concentrations of precursors of individual actinides, actinide mixtures, lanthanides and actinide/lanthanide mixtures, expressed as oxides, in the nitrate solution is between 250 and 500 g/L.
7. A method for obtaining monoliths using the method of claim 1, comprising adding to the nitric solution or suspension of actinides and

lanthanides, metals and non-metals of step i), a glass, glass-ceramic or ceramic matrix in the form of a powder with a particle size in the range of 1-100 pm,

ii) adding to said nitric solution or suspension of step i) at least one monomer or polymer with acrylonitrile (C_3H_3N) functional groups,

iii) thermal treating the nitric solution or suspension from step ii) in an air atmosphere at a temperature between 185°C and 225°C to obtain nanoparticles of actinide and lanthanide oxides,

iv) sintering at temperatures in the range of 610-825°C or melting at temperatures in the range of 1100-1300°C the mixture resulting from step iii) in an air atmosphere at atmospheric pressure, and in case of sintering,

v) uniaxially compacting at room temperature to form a monolith.

8. The method according to claim 6, wherein the glass matrix is powdered alumina-borosilicate glass in a mass ratio of oxides in the range from 1:1 to 9:1.

9. A method for obtaining monoliths according to claim 7, wherein step v) is carried out at room temperature.

10. The method according to claim 7, wherein the thermal treatment is carried out at a constant heating rate, starting from room temperature (20°C) or up to 75°C, reaching 225°C in less than 2 hours.

11. The method according to claim 10, wherein the thermal treatment is carried out at a heating ramp of 1.8-10°C/min.

12. The method according to claim 7, wherein the monomer or polymer with acrylonitrile (C_3H_3N) functional groups has a molecular weight of the repeating unit between 53.06 g/mol and 150000 g/mol for a typical polymer chain and has between 2000 and 5000 acrylonitrile groups, preferably about 3000 acrylonitrile groups.

13. The method according to claim 7, wherein the concentrations of precursors of individual actinides, actinide mixtures, lanthanides and

actinide/lanthanide mixtures, expressed as oxides, in nitrate solution are between 250 and 500 g/L.

14. The method according to claim 7, wherein the monolith is a tablet or pellet and the size of the nanoparticulated ash obtained in step iii) is from 5 to 100 nm.

15. The method according to claim 14, wherein the method also comprises the addition of oxides or nitrates of neutronic poisons selected from gadolinium, samarium, europium and erbium, to the nitric solution or suspension of step i) to obtain fuel tablets or pellets with burnable poisons.

16. The method according to any one of claims 1-15, for preparing nanoparticulated catalysts.

17. The method according to any one of claims 1-16, wherein the nitrates and oxides of actinides and lanthanides, metals and non-metals are selected among nitrates and oxides of Rb, Sr, Y, Ag, Cd, Cs, Ba, Ce, U, Fe, Zr, Ni, Sn, La, Pr, Nd, Sm, Eu, Gd, Cr, P, Se, U, Te, Rh, Ru, Mo, Th, uranium-thorium mixtures, and/or mixtures of these actinides with burnable poisons such as gadolinium, samarium, europium, and erbium.

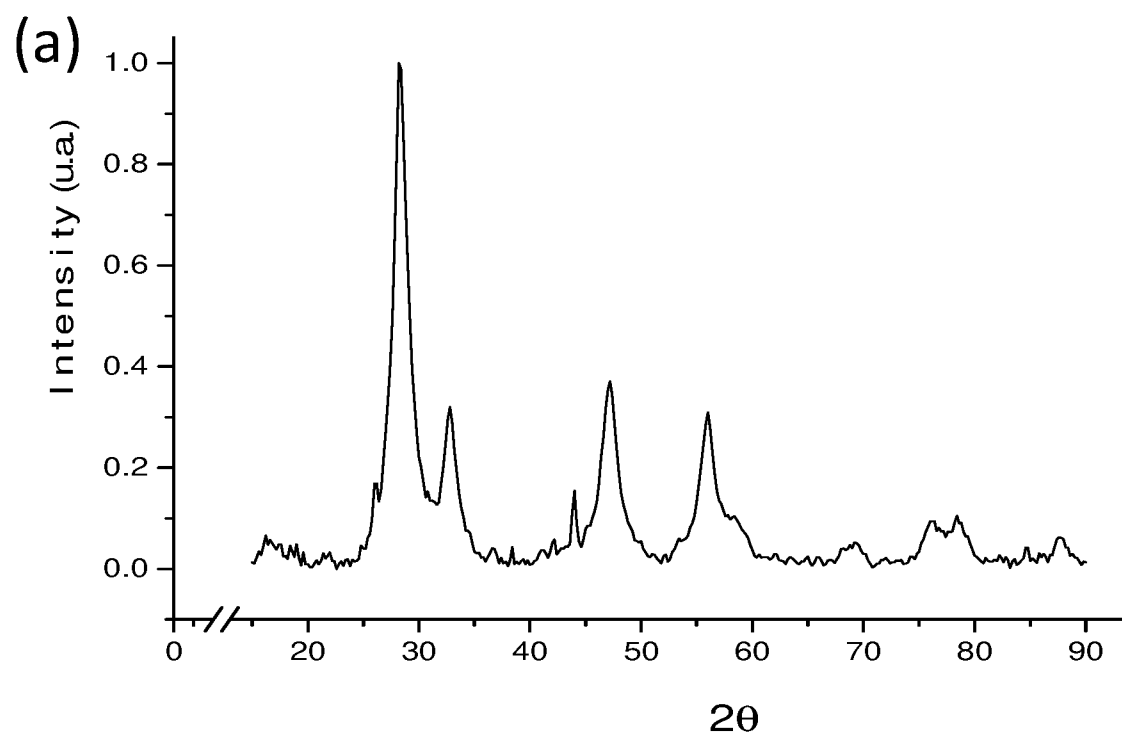


FIG. 1a

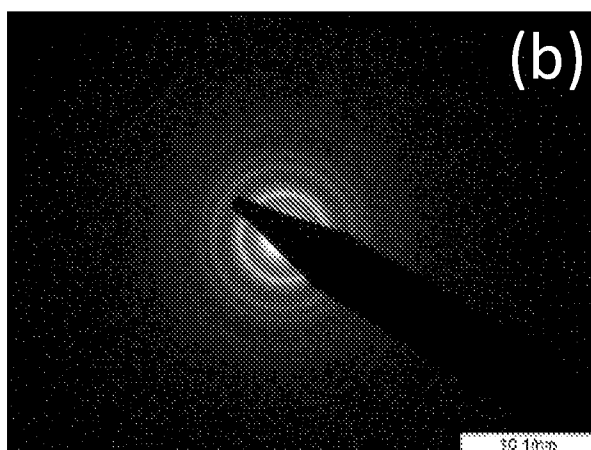


FIG. 1b

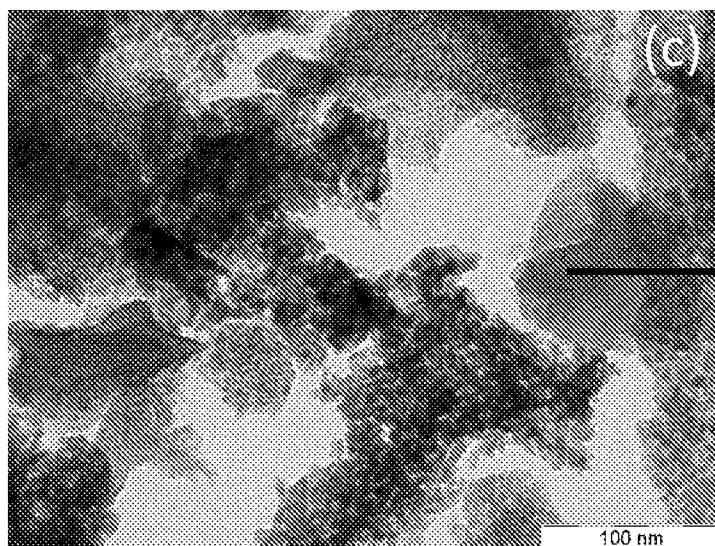


FIG. 1c

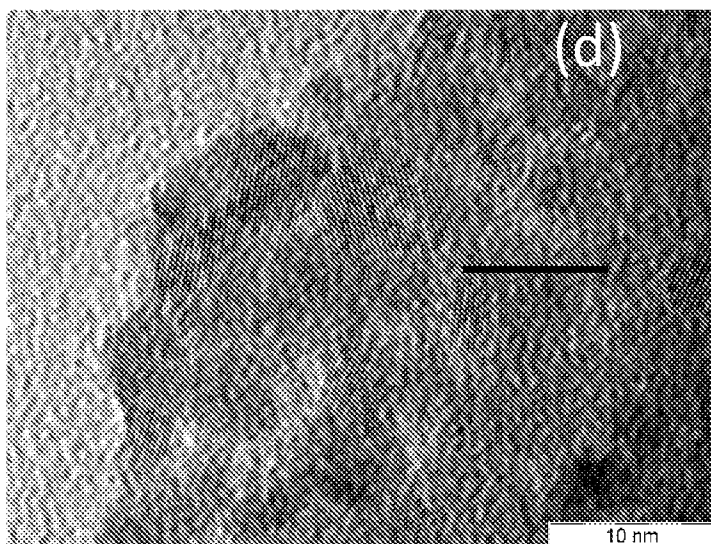


FIG. 1d

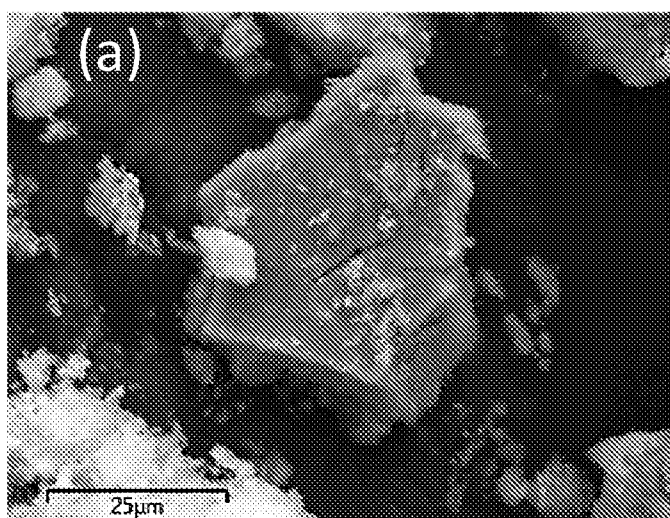


FIG. 2a

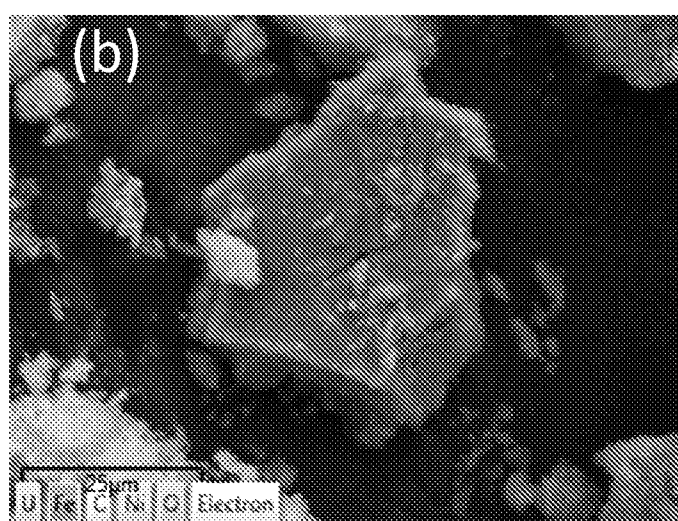


FIG. 2b

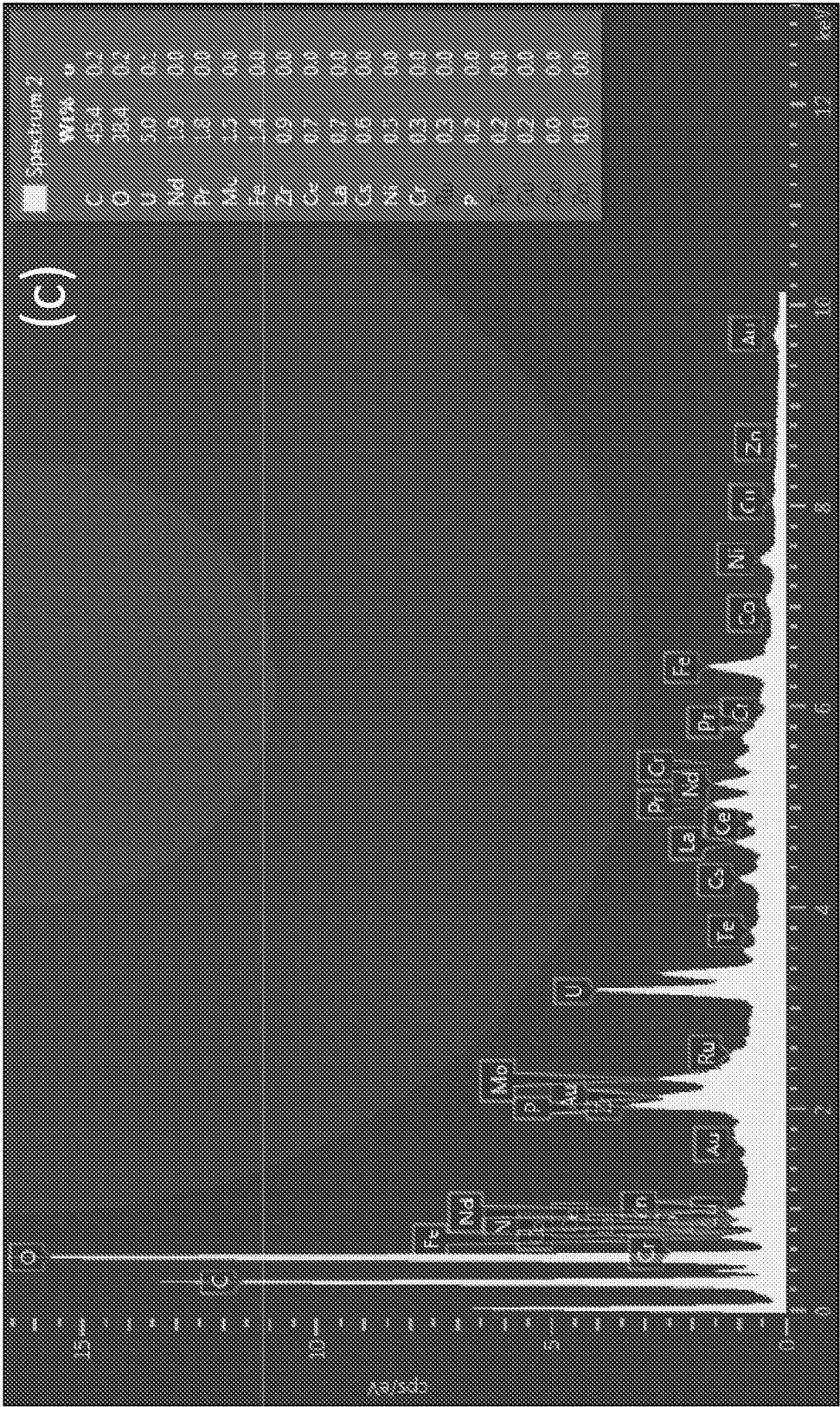


FIG. 2c

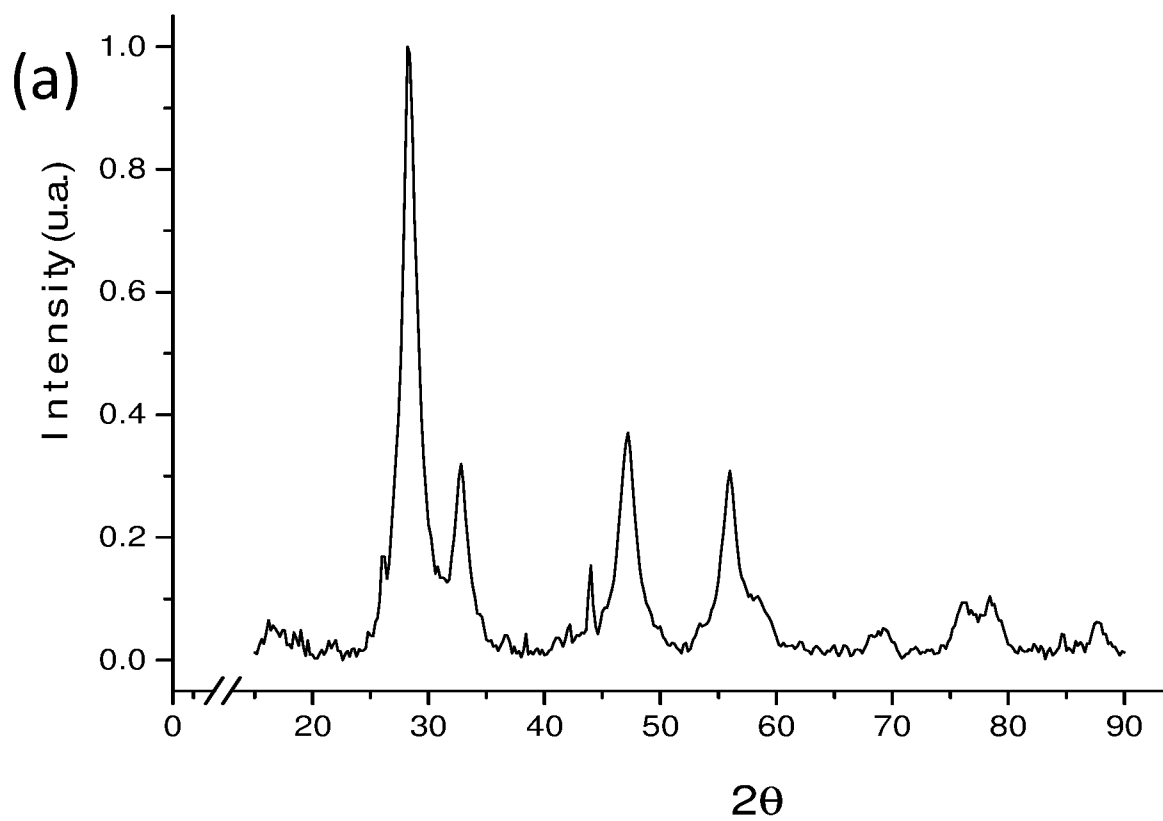


FIG. 3a

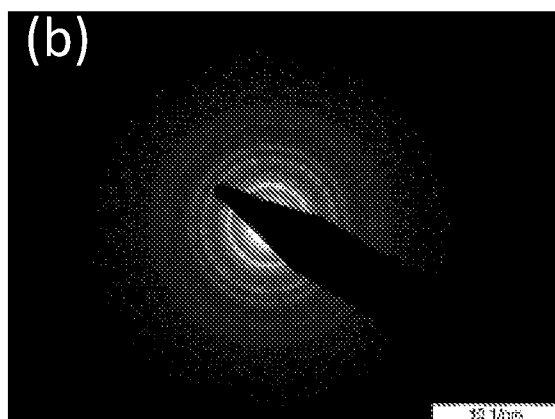


FIG. 3b

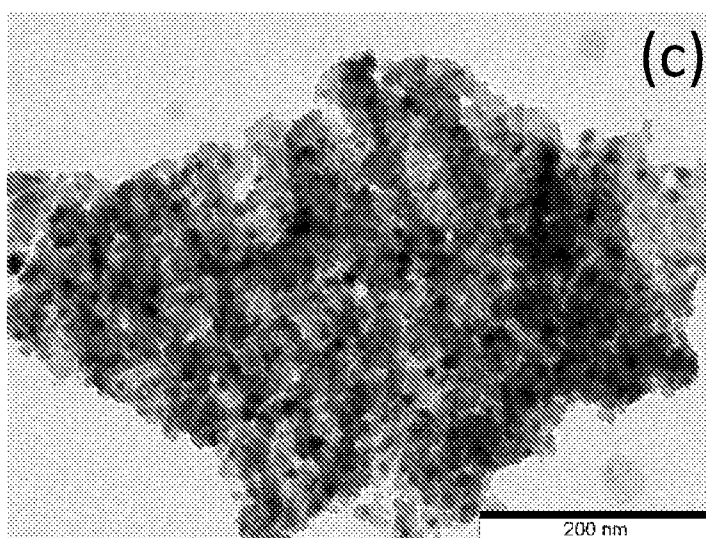


FIG. 3c

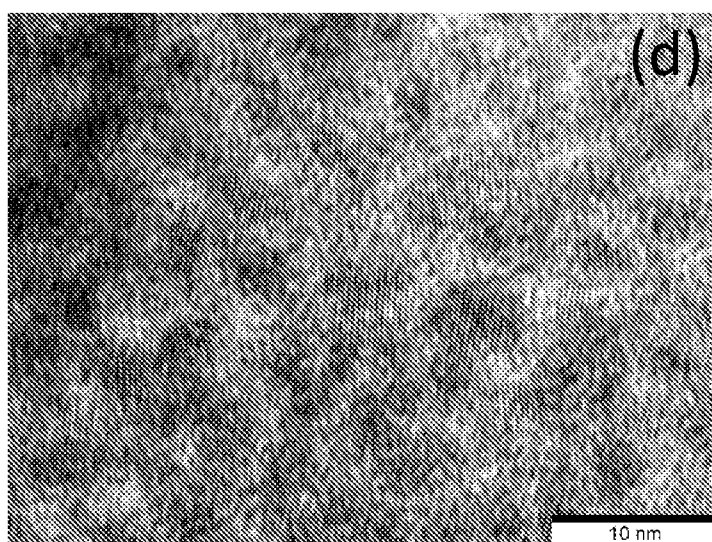


FIG. 3d

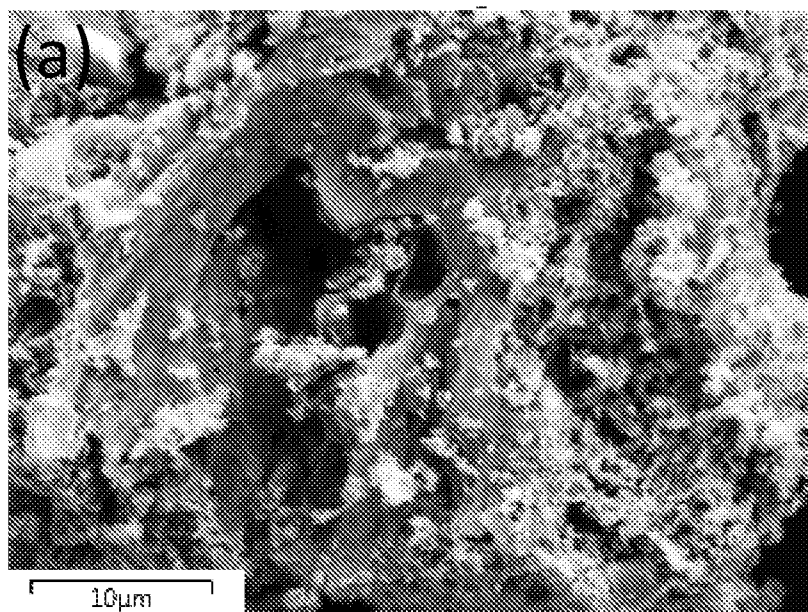


FIG. 4a

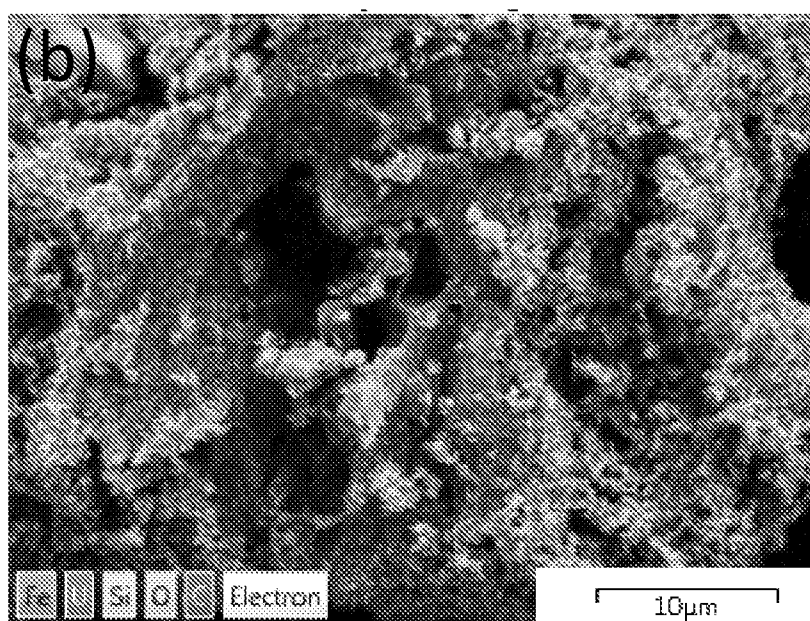


FIG. 4b

(c)

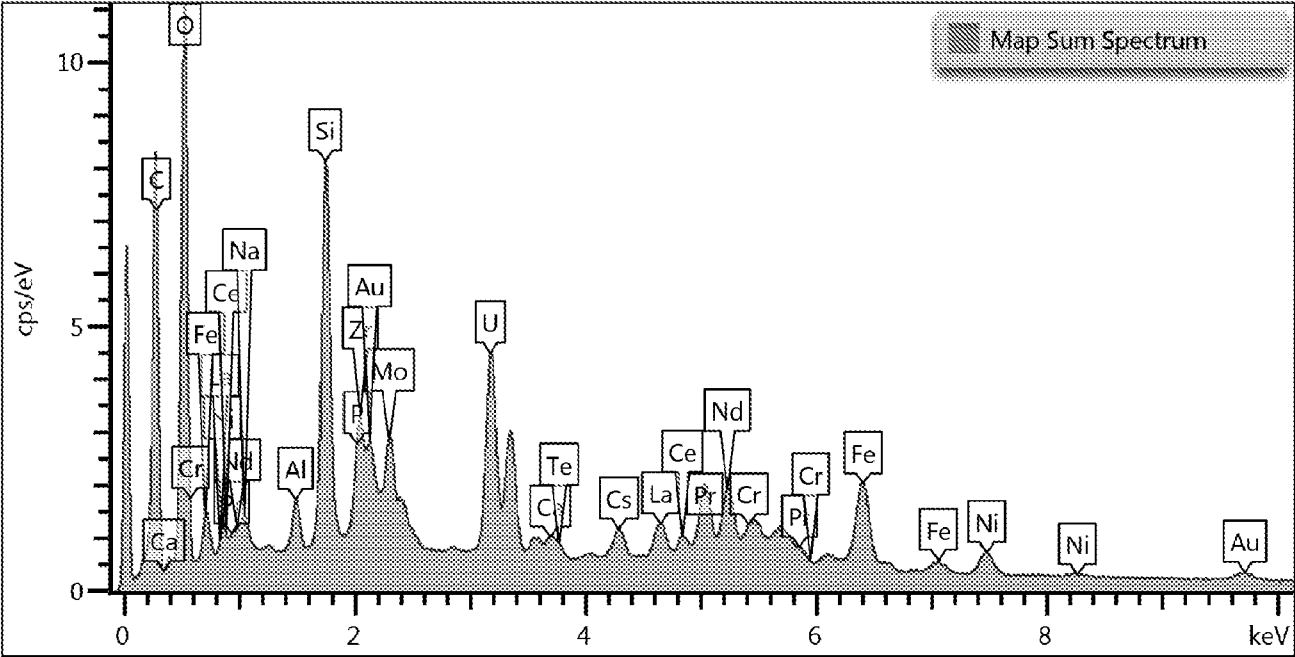


FIG. 4c

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2020/055461

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01F17/235 C01G43/01
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01F C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 936 348 A1 (COMMISSARIAT ENERGIE ATOMIQUE [FR]) 26 March 2010 (2010-03-26) thermal treatment 200-500C; page 21 - page 25; examples 1-2 -----	1-17
A	EP 3 034 483 A1 (COMMISSARIAT À L'ÉNERGIE ATOMIQUE ET AUX ÉNERGIES ALTERNATIVES [FR]) 22 June 2016 (2016-06-22) example 1 -----	1-17
A	WO 2013/026851 A1 (COMMISSARIAT ENERGIE ATOMIQUE [FR]; PICART SEBASTIEN [FR] ET AL.) 28 February 2013 (2013-02-28) page 22 - page 25 ----- -/-	1-17

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 September 2020

Date of mailing of the international search report

02/11/2020

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
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Authorized officer

Timmermans, Michel

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2020/055461

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 3 072 822 A1 (COMMISSARIAT ENERGIE ATOMIQUE [FR]) 26 April 2019 (2019-04-26) Thermal treatment 800C; page 13 - page 14; example 1 -----	1-17
A	FR 3 072 823 A1 (COMMISSARIAT ENERGIE ATOMIQUE [FR]) 26 April 2019 (2019-04-26) Thermal treatment 800C; page 12 - page 13; example 1 -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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			WO 2019081840 A1	02-05-2019
