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(54) Method of disposal of radioactive waste in "synthetic rock"

Methode der Entsorgung radioaktiver Abfälle in "synthetischem Gestein"

Méthode de traitement des déchets radioactifs dans une « roche synthétique »

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Description

[0001] The subject of the invention is a method of the disposal of radioactive waste a modified sol-gel method by enclosing them in a stable crystallographic structures of synroc ceramic materials, especially the type of perovskite, otherwise "Synthetic Rock". Actually, in the era of expanding nuclear power controversy raises the problem of security of both nuclear power plants and radioactive waste disposal. The energy generated from nuclear power plants should be considered as safe, not aggravating the environment. To meet these requirements, it is necessary to seek solutions that enable transformation of dangerous radioactive waste into such a form that they can be safely stored. Radioactive wastes are materials containing in their composition of the radioactive elements, which further use is impossible or unprofitable.

[0002] Generally, waste stored in such a way as to ensure the protection of people and the environment, both in normal conditions, as well as radiological events. The main task of processing technology and soldification of radioactive waste is to reduce their volume and to reduce the radioactivity and striving to obtain a product with the features that are most favorable from the point of view of their long-term storage. The main methods of radioactive waste solidification are: vitrification, asphalting, concreting, solidifying in epoxy resin as well as urea-formaldehyde and in materials type of synroc. A.E. Ringwood, based on previous observations and studies of the rocks, first used the term "synroc materials" that were used to solve the problems of disposal of radioactive waste.*A.E. Ringwood "Safe Immobilization of High Level Nuclear Wastes". Australian National University Press, Canberra, Australia, 1978 ,* A. E. Ringwood "Immobilization of Radioactive Wastes in SYNROC" American Scientist, vol 70, 1982, pp.201-207.

[0003] Synroc is a kind of "synthetic Rock" created for the safe storage of radioactive waste. This is an advanced ceramics consisting of geochemical stability of titanium compounds, which naturally occur in the earth's crust. They allow the incorporation in its structure almost all the radioactive the high-level (HLW-High Level Wastes) extracted from spent fuel, depending on the type and form of wastes. Synroc can take various forms. Based on the research highlights, there are some B, C, E, F synroc, depending on the type of ceramic matrix. And so, in the synroc-C there are three components; hollanite, zirconolite and perovskite. This material was designed to disposal of waste from reprocessing of spent fuel elements used in reactors and containing 10% up to 20% of HLW. The literature reference * A.T. Bukat "Application of multiphase ceramic materials to the disposal of radioactive materials", Bioprojectgrup, Via Giuilia 67 Roma, Italia, the basis for the entire family of ceramic multiphase materials type of Synroc is titanium compounds obtained by melting and crystallization.

[0004] Frequently described in the literature method of immobilization of HLW waste in materials type Synroc is synthesis in a solid phase - "solid-state reaction" - preparation of titanium compounds, namely a matrix to which are added the radioactive waste elements. The final stage of the process is compressed under high pressure and long hours (20h) conversion of the final product in the high temperature. So it is a very complex, time-consuming and economically unprofitable process.

[0005] Searching for alternative solutions in order to eliminate the above-mentioned problems and to reduction of costs in many scientific works, appeared a number of studies based on known literature synthesis involving wet liquid-liquid methods, especially a sol-gel method. * A.E. Ringwood, V.M. Oversby, S.E. Kesson, W. Sinclair, N. Ware, W. Hibberson, A. Major "Immobilization of high-level nuclear reactor wastes in SYNROC: A current appraisal" Nuclear and Chemical Waste Management, Volume 2, Issue 4, 1981, Pages 287-305.

[0006] While in available literature, there are no information about the trial recessed radioactive elements to the materials type Synroc - perovskite in the modified synthesis based on the use of ascorbic acid, in other words a complex of the sol-gel-CSGP. This method has been used successfully for the preparation of various compounds but never to synthesize such a complex crystallographic form as Synroc type perovskite with built-in radioactive element in order to dispose of HLW waste. The literature listed below refer to the use of CSGP to receive various types of compounds, but never for the preparation of materials with such a complicated structure as Synroc while disposing of the radioactive waste in this structure [1-4].

[0007] The use of ascorbic acid in combination with radioactive metal nitrates is known e.g. from D2. It is however noted that D2 does not give any hint with respect to the use of $Ti(NO_3)_4$, since D2 aims the disposal of radioactive waste in the form of glasses and not in the form of synroc.

[0008] It is also known from patent PL198039 (A.Deptula, W.Lada, T.Olczak, A.G.Chmielewski, S.Casadio, C.Alvani, F.Croce, "Method obtain titanium dioxide and Titanium tetrachloride with lithium and tytanite") method of obtaining a sol $Ti(NOs)_4$ from a sol constituting a solution of titanium tetrachloride $TiCl_4$ by distillation under vacuum, with the addition of concentrated nitric acid in a volume ratio of 1:1, where then produced, chloride-free colloidal solution of Ti^{4+}, evaporated to dryness and calcined. This method can be used to obtain the starting sol Ti^{4+} and then to obtain perovskite type synroc by the method of the invention, which is defined in the appended claims.

[0009] Unexpectedly, the process according to the invention allows for disposal of a radioactive waste type HLW while receiving Synroc perovskite-type, in one of the modified sol-gel synthesis.

[0010] Unexpectedly, other studies have shown that the CSGP method can successfully be applied to all elements contained in HLW as well as other contained in the radioactive waste. In the method according to the invention, directly to the crystallographic structure can be incorporated radioactive element already during the formation of the sol, leading to a homogeneous distribution of radioactive elements in the structure of the final product.

[0011] Also unexpectedly, the advantage of the method according to the invention, in the preparation of Synroc with integrated radioactive element, is not only the abovementioned homogeneity, but also reduces of the sintering temperature and the increased resistance of Synroc with integrated radioactive element to external influences, especially to leaching (elution during waste storage).

[0012] A method of the immobilization of radioactive waste in a synthetic Synroc rock type perovskite by incorporating in its structure elements of radioactive waste, according to the invention, is provided in claim 1.

[0013] In the present invention, obtained artificial rock subjected to XRD and IR analysis, and the resulting precursor of synroc is pelletized and calcined at a temperature o 1200°C for 2h.

[0014] Preferred embodiments are defined in the dependent claims.

[0015] The temperature and the time of conversion to synroc type perovskite was determined during own research termogravimetrically.

[0016] In order to verify the purity and the structure thus obtained synroc was subjected to XRD and IR analysis. Thus obtained precursor powder of synroc type perovskite with integrated calcium was pelleted and sintered at 1200°C for 2h.

[0017] In the current energy situation, not only in the Poland but also in the world, when it returns to nuclear energy, one of the most important issues in environmental protection is permanent disposal of radioactive waste type HLW during their utilization and storage as well as minimizing the costs of their disposing for a long period of time (resistance on the impact of external factors). Therefore, undeniable advantage of the present invention is the simplified way of conducting the synthesis of the final product which is perovskite-type synroc, which meets all of the criteria and required above.

[0018] Studies of the X-ray structures have shown that in the resulting material are not characteristic range of metal oxides, they are a perovskite-type structures of synroc, and the results of research in the infrared showed no contamination.

[0019] All experiments were performed by using surrogates of a high-level radioactive elements contained in HLW waste.

[0020] The invention is illustrated by the following examples.

Example I.

[0021] For the preparation of chloride-free colloidal solution Ti^{4+}dechlorination was carried out five times, by measuring out 100ml of 99,9% solution $TiCl_4$ (from Aldrich Chemical Corporation), in which the titanium concentration was 183g Ti^{4+}/l, and chlorine was 465g Cl^-/l. The solution was placed in a rotary flask, in a water bath of vacuum device type Rotavapor (Buchi). In order to dechlorinate, was sucked under vacuum portions of 5ml of 200ml of concentrated HNO_3 to solution of $TiCl_4$ in concentrated hydrochloric acid at 80°C. After entering of all of the nitric acid solution changed its color from yellow to orange. The process continued until 200ml of the solution was evaporated. In the distillate content of chlorides was studied, using a solution of $AgNO_3$. Precipitation of a white precipitate indicated a high chloride content. Therefore, dechlorination operation was repeated five times, each time by adding 200ml of nitric acid, interrupting each process after obtaining 200ml of distillate. After each stage content of chlorides was checked, until when in the sample was no precipitate formed. During the next stages of the the process, solution in the flask became turbid and at the end to get the milky-white color. Thus obtained chloride-free, colloidal solution of $Ti(NO_3)_4$, which is a starting solution for the preparation of titanates, which are the basis of the family of ceramic multiphase materials type Synroc. Thus obtained colloidal solution of $Ti(NO_3)_4$ was placed back into the Rotavapor evaporator machine in special container adapted to receive powder, to which was added (by sucking in) ASC ascorbic acid [L-Ascorbic Acid (E300) USP/Ph.Eur.] in an amount of 0.1 relative to the sum of moles of metals dissolved in 50ml of H_2O. Because colloidal solution of $Ti(NO_3)_4$ during the addition of ASC is churned very intensely, addition was carried out in small portions with vigorous stirring. Then the calcium carbonate cz.d.a. (PolskieOdczynnikiChemiczne, Gliwice) was added in the form of a slurry of 3% excess over the calculated stoichiometric amount to be able to develop $CaTiO_3$ i.e. 39.41 g in 150mL of H_2O, after calcination at a temperature of 170°C during 24h. Thus obtained sol was dried in vacuum for 1 h at 80°C to give white-yellow gel, which was given to heat treatment after the thermogravimetric analysis, by using Hungarien MOM Derivatograph, intended to provide temperature of each phase transition to the final product. The gel was dried in the oven for 24 h at 110°C, while calcining and sintering was carried out in an oven type CSF 1200 (Carbolitte Furnaces, England) at 450°C, 700°C. The residence time at each temperature is 2h and the speed of heating to the desired temperature was 2°C/min. Physico-chemical properties of the final product was analyzed by scanning microscope (Zeiss DSM 942) diffraction by using RigakuMiniflexdiffractometer with Cu-Kα radiation and a spectrometer for IR test (Bruker-Equinox 55). Thus obtained precursor powder of type perovskite synroc with integrated calcium was pelleted and sintered at 1200°C during 2h and subjected to a leaching water and the acidified water in order to verify resistance to adverse environmental conditions. The study was conducted over 30 days to give a negative result for Ca in the eluate (water leaching), which confirmed that the obtained end product meets the requirements of a materials synroc type.

Example II.

[0022] For the preparation of the perovskite-type of synroc with built into its structure model element to radioactive waste which is strontium, in the first stage sol $Ti(NO_3)_4$ is obtained as described in the Example I, and (in the same amount) ascorbic acid ASC is added, as also described above. To thus obtained starting sol in the form of a slurryis added, (sucks after dissolved in 150ml of H_2O) 35.47 g of calcium carbonate and 5.64g of strontium carbonate $SrCO_3$ in a molar ratio of 10% by mol of strontium, thereby replacing 10% by mol of calcium. The process is carried out under vacuum for 1h at 80°C to obtain a white gel and then proceed of thus obtained material as in the Example I. The XRD and IR analysis confirmed that the obtained material is synroc with integrated surrogate of strontium and the research for resistance to adverse environmental conditions, as well as in the Example I, confirmed that the resulting end product meets the requirements of materials type synroc.

Example III

[0023] For the preparation of the perovskite-type synroc with built into its structure model element to radioactive waste which is cobalt, in the first stage sol $Ti(NO_3)_4$ is obtained as described in the Example I, and (in the same amount) ascorbic acid ASC is added, as also described above. To thus obtained starting sol in the form of a slurry's added (sucks after dissolved in 150ml of H_2O) 35.47 g of calcium carbonate and 16.9 ml of cobalt nitrate $Co(NO_3)_2$ at a concentration of 133.3 g Co/l in a molar ratio of 10% by mol of cobalt, thereby replacing 10% by mol of calcium. The process is carried out under vacuum for 1 h at 80°C to obtain a white-yellow gel and then proceed of thus obtained material as in the examples above. The XRD and IR analysis confirmed that the obtained material is synroc with integrated surrogate of cobalt and the research for resistance to adverse environmental conditions, as well as in the Example I and Example II, confirmed that the resulting end product meets the requirements of materials type synroc.

Example IV

[0024] For the preparation of the perovskite-type synroc with built into its structure model element to radioactive waste which is cesium, in the first stage sol $Ti(NO_3)_4$ is obtained as described in the example above, and (in the same amount) ascorbic acid ASC is added, as also described above. To thus obtained starting sol in the form of a slurry's added (sucks after dissolved in 150ml of H_2O) 35.47 g of calcium carbonate and 14.90 g of cesium nitrate $CsNO_3$ in a molar ratio of 10% by mol of cesium, thereby replacing 10% by mol of calcium. The process is carried out under vacuum for 1 h at 80°C to obtain a pale-pink gel and then proceed of thus obtained material as in the examples above. The XRD and IR analysis confirmed that the obtained material is synroc with integrated surrogate of cesium and the research for resistance to adverse environmental conditions, as well as in the Examples I-III, confirmed that the resulting end product meets the requirements of materials type synroc.

Example V

[0025] For the preparation of the perovskite-type synroc with built into its structure model element to radioactive waste which is neodymium, in the first stage sol $Ti(NO_3)_4$ is obtained as described in the example above, and (in the same amount) ascorbic acid ASC is added, as also described above. To thus obtained starting sol in the form of a slurry's added (sucks after dissolved in 150ml of H_2O) 35.47 g of calcium carbonate and 4.29 g of neodymium oxide Nd_2O_3 in a molar ratio of 10% by mol of neodymium, thereby replacing 10% by mol of calcium. The process is carried out under vacuum for 1 h at 80°C to obtain a white-beige gel and then proceed of thus obtained material as in the examples above. The XRD and IR analysis confirmed that the obtained material is synroc with integrated surrogate of neodymium and the research for resistance to adverse environmental conditions, as well as in the Examples I-IV, confirmed that the resulting end product meets the requirements of materials type synroc.

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[0026]

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Claims

1. A method of the immobilization of radioactive waste in a synthetic rock , synroc, by incorporating in its structure elements included in the high-level radioactive waste, comprising the steps in the following order:

    - preparing a chloride-free solution of colloidal sol, preferably $Ti(NO_3)_4$,
    - adding ascorbic acid ASC as complexing compounds in relative from 0.1 to 0.3, to the sum of the moles of radioactive elements contained in the radioactive waste in the form of carbonates or nitrates of metals selected from strontium, cobalt, cesium and neodymium,
    - introducing calcium carbonate in slurry form with an excess of 1% to 5%, preferably 3% by mol, relative to the calculated stoichiometric amount to be able to develop $CaTiO_3$,
    - adding selected radioactive elements contained in the radioactive waste in a molar ratio of 2% to 14%, preferably 10% by mol, of the metals, thereby replacing 2% to 14% by mol, preferably 10% by mol, of the previously introduced amount of calcium,
    - evaporating and drying the thus obtained sol,
    - subjecting the sol to thermal treatment to obtain a precursor of synroc with integrated radioactive elements,
    - subjecting the precursor to XRD and IR analysis, and
    - pelletizing and calcination of the precursor at a temperature of 1200°C for 2h.

2. A method according to claim 1, wherein the chloride-free sol $Ti(NO_3)_4$ is obtained from a solution of titanium tetrachloride in concentrated hydrochloric acid, by several times, preferably five times, stripping of chloride by vacuum distillation, with adding in each case concentrated nitric acid in a volume ratio 1:1.

3. A method according to claim 1, wherein the step of evaporating and drying of the obtained sol, which is a precursor of perovskite synroc in the form of a slurry, comprises evaporation of the obtained sol at 80°C under vacuum for 1 h to obtain a white-yellow gel, which is then dried in an oven at 110°C for 24h and subjected to heat treatment at 450°C and 700°C in equal time spent in various temperature for 2h and a heating rate of 2°/min.

Patentansprüche

1. Verfahren zur Entsorgung radioaktiver Abfälle in dem "synthetischen Felsen", Synroc, indem in ihre Struktur die Elemente eingebaut werden, die ein Bestandteil der hochradioaktiven Abfälle sind, umfasst die Schritte in der folgenden Reihenfolge:

    - Vorbereitung der kolloidalen Lösung von Sol $Ti(NO_3)_4$, ohne Chloride,
    - Hinzufügen der ASC Ascorbinsäure als komplexbildende Verbindung in dem Verhältnis von 0.1 bis 0.3, zur der Summe der Mole an radioaktiven Elementen, die in dem radioaktiven Abfall in Form von Carbonaten und Nitraten von gewählten Metallen aus Strontium, Kobalt, Cäsium und Neodym enthalten sind,
    - Einführung von Calciumcarbonat in Form von der Suspension mit einem Überschuss von 1% bis 5%, günstig 3% im Verhältnis zu der berechneten stöchiometrischen Menge, damit der $CaTiO_3$ entstehen kann,
    - Hinzufügen von einigen radioaktiven Elementen, die im radioaktiven Abfall in einem Molverhältnis von 2% bis 14% enthalten sind, günstig 10%, der jeweiligen Metalle, indem von 2% bis 14%, günstig 10% der vorher eingeführten Menge von Calcium,
    - auf diese Weise entstandenes Sol verdampft und trocknet
    - Sol wird der Wärmebehandlung unterzogen, um den Vorläufer von Synroc mit radioaktiven eingebauten Elementen zu erzielen,
    - der Vorläufer wird der Analyse XRD und IR unterzogen,
    - dann wird der Vorläufer pelletisiert und in der Temperatur 1200°C in der Zeit von 2h kalziniert.

2. Verfahren gemäß des Anspruchs 1, **gekennzeichnet dadurch, dass** es Sol $Ti(NO_3)_4$ ohne Chloride aus einer Lösung von Titantetrachlorid in konzentrierter Salzsäure durch mehrfaches, vorzugsweise fünfmaliges, Abstreifen der Chloride mittels der Vakuumdestillation erhalten wird, indem es jeweils konzentrierte Salpetersäure von einem Volumenverhältnis von 1:1 hinzugefügt wird.

3. Verfahren gemäß des Anspruchs 1, **gekennzeichnet dadurch, dass** der Schritt der Verdampfung und Trocknung des erhaltenen Sols, das Vorläufer von synrocu perovskite in Form von der Suspension ist, aus der Verdampfung bei der Temperatur von 80° C unter dem Vakuum besteht, es dauert 1 h, bis das gelb-weiße Gel erhalten wird, das dann in einem Trockner in der Temperatur von 110°C innerhalb von 24h getrocknet wird, und das einer Temperaturbehandlung von 450°C und 700°C in der gleichen Verweilzeit in jeweiligen Temperaturen nach 2h und der Heizrate von 2°/Min unterzogen wird.

Revendications

1. Méthode d'élimination des déchets radioactifs dans une "roche syntéthique", synroc, en incorporant dans sa structure des éléments faisant partie des déchets radioactifs de haute activité qui comprend des étapes suivantes :

   - préparation de la solution de chlorure de sol colloïdale $Ti(NO_3)_4$
   - ajout de l'acide ascorbique ASC en tant que produit complexant, rapport de 0,1 à 0,3 au nombre total de moles des éléments radioactifs inclus dans les déchets radioactifs sous forme de carbonates et de nitrates des métaux choisis parmi le strontium, le cobalt, le césium et le néodyme,
   - incorporation du carbonate de calcium sous forme de suspension avec un surplus de 1% à 5%, préférablement 3% molaires par rapport à la quantité stoechiométrique calculée pour pouvoir créer $CaTiO_3$,
   - ajout des éléments radioactifs choisis inclus dans les déchets radioactifs selon un rapport molaire de 2% à 14% molaires, préférablement 10% molaires, des différents métaux en remplaçant ainsi de 2% à 14% molaires, préférablement 10% molaires de la quantité du calcium introduite préalablement,
   - sol ainsi reçu passe au processus d'évaporation et de séchage
   - sol est subi au traitement thermique afin d'obtenir un précurseur du synroc avec des éléments radioactifs incorporés,
   - précurseur est subi à l'analyse XRD et IR,
   - ensuite, le précurseur est granulé et calciné à 1200°C pendant 2 heures.

2. Dans la méthode selon la réserve N°1, il en est significatif que le sol XXX $Ti(NO_3)_4$ est utilisé et est reçu de la solution du Tétrachlorure de titane dans l'acide chlorhydrique concentré en chassant quelques fois, préférablement 5 fois, les chlorures grâce à la méthode de distillation sous vide, en ajoutant à chaque fois l'acide nitrique (rapport de volume 1:1).

3. Dans la méthode selon la réserve N°1, il en est significatif que l'étape d'évaporation et de séchage du sol reçu étant le précurseur du synroc perovskite, sous forme de suspension, comprend les phases suivantes : évaporation à 80°C, sous vide, pendant 1 heure jusqu'à la réception du gel blanc-jaune qui est ensuite séché à 110°C pendant 24 heures dans une sécheuse, le gel est après subi au traitement thermique à 450°C et 700°C, même durée pour les deux températures (2 heures) et vitesse de chauffage 2°/min.

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