



# New generation of nuclear fuels: Stability of different stearates under high doses gamma irradiation in the manufacturing process



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## HIGHLIGHTS

- Dose deposition estimation for different stearates.
- Stearates radiolysis and radio-oxidization at high doses using gamma-rays.
- H<sub>2</sub> emission estimation as a function of atmosphere and dose.
- Chemical modifications in stearates as a function of atmosphere and dose.
- Comparison of three stearates.

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## ABSTRACT

In the future reactors, the pellets radioactivity will increase due to the modification of the plutonium concentration. The stability of the organic additive used as lubricating/deagglomerating agent has thus to be evaluated. Up to now, zinc stearate is employed, but new additives are tested in this study and compared to zinc stearate. In a first part of this paper, the order of magnitude of the dose deposited in the stearates has been estimated. Afterward, three different stearates have been irradiated, using gamma-rays at doses as high as 2000 kGy. Two atmospheres of irradiation were tested, *i.e.* inert atmosphere and air. Samples were characterized using the following analytical tools: mass spectrometry, thermogravimetry and infrared spectroscopy. The objective is the evaluation of the ageing of these materials. In the nuclear fuel pellets manufacturing context, the candidate which could replace zinc stearate, if this one is too degraded to fulfill its role of lubricant in the pellets of the future manufacturing, has been determined.

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## 1. Introduction

The manufacturing process of nuclear fuels is based on a powder metallurgy process which includes the steps of grinding, pelletizing and sintering. One or more of these steps implement the addition of organic molecules in order to lubricate and/or deagglomerate pellets.

The purpose of the grinding step is to reduce the particles sizes, but also, in the case of mixing different powders to homogenize them. In the nuclear industry, a ball mill is generally employed, but

its efficiency can be low if the finest particles reaggregate. To counteract this phenomenon, a chemical additive is added at the same time as the solid, to deagglomerate the powder. The chemical additive added in these conditions can be of the families of phosphates, ferrocyanides, stearates, silicates, aluminosilicates...

The second step in the production of the fuel pellets is the pelletizing. The powder is poured into the industrial mold and then compacted to form a coherent pellet that is ejected from the matrix. The powder compression involves the effects of friction between the powder and the matrix on one hand, and between the particles on the other hand. Indeed, the frictions are responsible for a heterogeneity of density distribution in the material. Consequently, the addition of a molecule having a lubricating function makes possible, during this stage, to reduce the friction forces and leads to

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the preparation of more homogeneous pellets, with a better quality and in a reproducible manner.

The elimination of the lubricating and/or deagglomerating agent, called debinding, is one of the critical steps of the nuclear fuel production process [1]. Indeed, if it is not well managed, it can generate defects (internal stress, crack, deformation) that will be detrimental to the final properties. The most commonly used debinding technique is the thermal one, which results in the decomposition of the organic additive into volatile species which are removed by gas-phase transport.

Up to now, zinc stearate (StZn) is the organic additive used in the production of nuclear pellets to be irradiated in Pressurized Water Reactors (PWR), those in pure UO<sub>2</sub> and those in MOX (PuO<sub>2</sub> and UO<sub>2</sub> mixtures, with Pu content of less than 12%). StZn is employed as deagglomerating and lubricant agent. This organic molecule is introduced at 0.1 %wt in the grinding step and then at 0.3 %wt prior to pelletizing. Its thermal decomposition occurs with gas emission and formation of a solid residue, ZnO. The elimination of ZnO can then be obtained under reducing atmosphere (gas Ar-H<sub>2</sub> with 5 %vol): ZnO is reduced in Zn and the metal evaporated at about 900°C, its boiling point.

In the development of the future reactors (generation IV) context, fuels will be loaded with an increased content of Pu (target content of approximately 30%), and the Pu employed will present isotopes with higher specific activity like <sup>238</sup>Pu. With these modified nuclear fuels pellets, the temperature inside the pellets and the deposited dose in the additives will increase. The understanding of the resistance to thermolysis and radiolysis of the organic additives employed in such a manufacturing process becomes crucial.

As StZn has a relatively low thermal stability, two other molecules are currently tested to potentially replace StZn. Calcium and lithium stearates, respectively StCa and StLi, have been chosen because of their higher thermal stability compared to StZn [2]. Magnesium stearate (StMg), already studied in the context of nuclear waste pelletizing [3], has shown a thermal stability lower than the one of StZn, and so, has not been retained in this study.

Calcium stearate has already been tested as lubricant for the pelletizing of nuclear fuels [4,5]. It has been shown that, first, StCa had to be dried at about 110°C during a few hours before use because of the presence of water retained in the organic powder [6], and second, this lubricant leaves CaO residues in the pellets after sintering, within the limit of the solubility of this molecules in the uranium and/or plutonium oxides. Nevertheless, the final concentrations remain compatible with the specifications for MOX fuel. StLi has the higher thermal stability but has never yet been tested as lubricant for the pelletizing of nuclear fuels.

The aim of this article is to compare the gamma-irradiation of different stearates: StZn, StCa and StLi. The materials have been irradiated up to high doses (2000 kGy) to simulate their ageing in the crude pellet, before sintering, in case of a temporary cessation of production for instance. The order of magnitude of the dose deposited in the stearates has been estimated using two different methods that are described in a first part of this article. Then, the effect of atmosphere of irradiation has been experimentally assessed. The objective is here to evaluate the modifications at a molecular level of the three different materials to understand better their behavior under irradiation and then in temperature. The aim is here to evaluate the potential use as lubricant of different stearates in the future nuclear fuel pellets process manufacturing.

## 2. Lubricant dose deposition determination

In the future, fuels will be loaded with an increased content of Pu. The deposited dose in the lubricant will thus increase, depending on the plutonium isotopy and on the auto-absorption

coefficient of the grain, *i.e.* of the size of each grain. This grain's size cannot be experimentally determined, especially in an industrial context. The first part of this article is thus devoted to the evaluation of the dose that will effectively receive the lubricating agent, *i.e.* stearate, in contact with the (U, Pu)O<sub>2</sub> grains.

The dose deposition in stearates by 1 g (U, Pu)O<sub>2</sub> mixture, containing an increased content of Pu, can be estimated using some approximations. The mixture chosen for the approximation is 70% UO<sub>2</sub> + 30% PuO<sub>2</sub> + 0.3% St. The oxide contains some americium but its activity represents less than 1% of the total activity: in the following Am is omitted. The activity of this mixture is comprised between 3 and 5.10<sup>11</sup> Bq/g<sub>oxide</sub>, depending on the Pu isotopy.

### 2.1. First method

If we consider a homogeneous mixture, the mean dose rate  $\bar{d}$  can be calculated using Equation (1).

$$\bar{d} = \frac{P_{released}}{m_{mixture}} \cdot \delta \quad (1)$$

With:

- $P_{released}$  the power released by the PuO<sub>2</sub> grains in W,
- $m_{mixture}$  the mass of the 70% UO<sub>2</sub> + 30% PuO<sub>2</sub> + 0.3% St mixture in kg,
- $\delta$  the correction factor applied to take into account the dilution effect of the mixture.

Stearate will not have the same Linear Energy Transfer (LET) than the mixture because of the difference in hydrogen concentrations. The factor  $\delta$  can be calculated from Equation (2):

$$\delta = \frac{LET_{\bar{E}_{emitted}}^{StZn}}{LET_{\bar{E}_{emitted}}^{mixture}} = \frac{LET_{\bar{E}_{released}}^{StZn}}{LET_{\bar{E}_{released}}^{mixture}} = \frac{\left(R_p^{mixture}\right)_{\bar{E}_{released}} \cdot \rho_{mixture}}{\left(R_p^{StZn}\right)_{\bar{E}_{released}} \cdot \rho_{StZn}} \quad (2)$$

Where:

- $LET_{\bar{E}_*}^k$  is the Linear Energy Transfer (of stopping power) of the alpha particles of energy  $\bar{E}_*$  in the material k, in MeV.mg<sup>-1</sup>.cm<sup>2</sup>,
- $\bar{E}_{emitted}$  is the mean energy emitted by the alpha particles,
- $\bar{E}_{released}$  is the mean energy released by the alpha particles,
- $(R_p^k)_{\bar{E}_*}$  is the path of the alpha particles of energy  $\bar{E}_*$  in the material k,
- $\rho_*$  is the molar mass of the material k.

In Equation (2),  $\delta$  is calculated from the last formula, using  $(R_p^k)_{\bar{E}_*}$  and  $\rho_*$ . The difference between  $\bar{E}_{emitted}$  and  $\bar{E}_{released}$  is that a part of the energy is lost in the grain itself. Hence, the self-absorption coefficient  $a_\alpha$  has to be calculated to estimate  $P_{released}$ .  $a_\alpha$  is directly a function of the distance covered by the alpha particle in the grain, *i.e.* directly a function of the radius of the particle, as it is shown on Fig. 1, on the left. Finally, it can be deduced Equation (3):

$$P_{released} = P_{emitted} \cdot (1 - a_\alpha) \quad (3)$$

The numerical tool SRIM, based on the TRIM code [7], was used to calculate the LET, and, using different incident energies, the path of the alpha particles in stearate and in UO<sub>2</sub>. Mixture of (U, Pu)O<sub>2</sub> was not simulated because Pu is not present in the SRIM code: we choose to simulate the (U, Pu)O<sub>2</sub> mixture by using UO<sub>2</sub> in the SRIM code. Finally, the dose rate  $d$  received by the organic additive can be estimated in function of the (U, Pu)O<sub>2</sub> grain radius. Results are given shown on Fig. 1, on the right.

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