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Chemical composition of inhalable MOX powders prepared according to a SOLGEL process: energy dispersive X-ray analysis of individual particles

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Abstract

We have characterized the homogeneity of inhalable $(U,Pu)O_2$ (MOX) powders made according to an experimental SOLGEL process by co-precipitation of soluble forms of U and Pu. These powders contained 5.3 wt.% Pu/U+Pu. In order to study inhaled particles, we have exposed rats to the MOX aerosol, and alveolar macrophages were extracted by pulmonary lavage 3 days later. Chemical analyses were performed on entire cells, using a scanning transmission electron microscope (STEM) at 200 kV interfaced with energy dispersive X-ray spectrometry (EDS). The raster analysis showed the particles contained 6.6% Pu (SD=0.9, n=20). The homogeneity was confirmed in a range of a few nanometers in each particle analysed by element mapping using a 7-nm nanoprobe. These results demonstrate that the chemical composition of the SOLGEL powders is 'homogeneous' enough, so that they could be used as reference compounds for the toxicological studies after inhalation exposure to industrial MOX powder. © 1998 Elsevier Science S.A.

Keywords: Lungs; Alveolar macrophage; Scanning transmission electron microscopy; Energy dispersive X-ray spectrometry; MOX

1. Introduction

Mixed (U,Pu) oxides (MOX) are more and more used as fuel in pressurized water reactors. These compounds are obtained by different processes including, before sintering, either a step of co-precipitation of soluble U and Pu referred to as the SOLGEL process [1] or blending fine particles of UO_2 and PuO_2, such as with the COCA or MIMAS processes recently developed for industrial purpose [2]. Only a few data on the biokinetics of transuranium elements are available after inhalation of MOX, which is the main route of potential contamination of workers involved during industrial processing. The results suggest that, after inhalation, the transfer of Pu to extrapulmonary organs was higher than that measured after inhalation of PuO_2 [3–5]. Moreover, this Pu transfer seemed to increase as the relative Pu fraction in MOX decreases [6]. Most of these experimental studies did not mention detailed information on the MOX fabrication process, and the way inhalable particles were obtained. Early studies have reported that MOX obtained by milling and sintering were solid solutions, as characterized both by X-ray diffraction and energy dispersive X-ray spectrometry (EDS) analysis [7]. By contrast, using EDS, we have recently reported that inhalable MOX particles recovered at the grinding step, which were made according to the COCA and MIMAS processes, were heterogeneous, i.e. single particles corresponded to either 'pure' UO_2, 'pure' PuO_2, or $(U,Pu)O_2$ containing Pu in a range up to 30% [8,9].

The aim of this work was to characterize the distribution of the amount of Pu in MOX powder containing 5.3 wt.% of Pu/U+Pu after inhalation in the rat. The MOX was prepared according to an experimental SOLGEL process, and the inhalable particles were obtained by a milling process.

2. Materials and methods

All experiments on animals were performed by scientists authorized by the French Ministry of Agriculture to carry out these procedures. A group of 30 male Sprague-Dawley rats was exposed at 3 months of age to MOX aerosols produced by nebulization of a powder suspension in water, using our inhalation facility as previously described [10]. The MOX made according to the SOLGEL process globally contained 5.3% of Pu/Pu+U. The Pu isotopic

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composition was 1.1% ^{238}Pu, 64.0% ^{239}Pu and 4.5% ^{241}Pu, expressed as weight percentage, and 7.9% of the total α activity was due to ^{241}Am. The initial lung burden in the range of 100–200 Bq (α emission) was measured 7 days after exposure by X-ray spectrometry of the living animals.

Three days after exposure, one animal was killed under pentobarbital anesthesia (40 mg kg^{-1}). Pulmonary lavage was performed by repeated instillation of 5 ml 0.9% NaCl until a total volume of 20 ml had been collected. Cytospins of the cell suspensions were prepared on collodion-coated slides, and cells were fixed for 30 min in 70% ethanol. For electron microscopy study, the collodion film was put on copper grids and coated with carbon as previously described [11]. Samples were observed with a CM 200 Philips microscope using the scanning transmission mode at 200 kV. The shape of particles was estimated at different tilt angles with respect to the beam direction under high-angle annular-dark field (HAADF) observation mode. The particle diameter distribution was measured using standard image analysis software developed in our laboratory. EDS analysis of the entire particle in alveolar macrophages was performed with an EDAX X-ray detector (super ultra-thin window). This was done by scanning over a rectangular field including the whole particle (raster analysis). Quantitative analyses were obtained with an EDAX software based on Cliff and Lorimer equations considering the same *K*-factor value for U and Pu [12]. These spectrum analyses were combined to specific Pu and U Lα X-ray mapping to provide element imaging using a 7-nm nanoprobe.

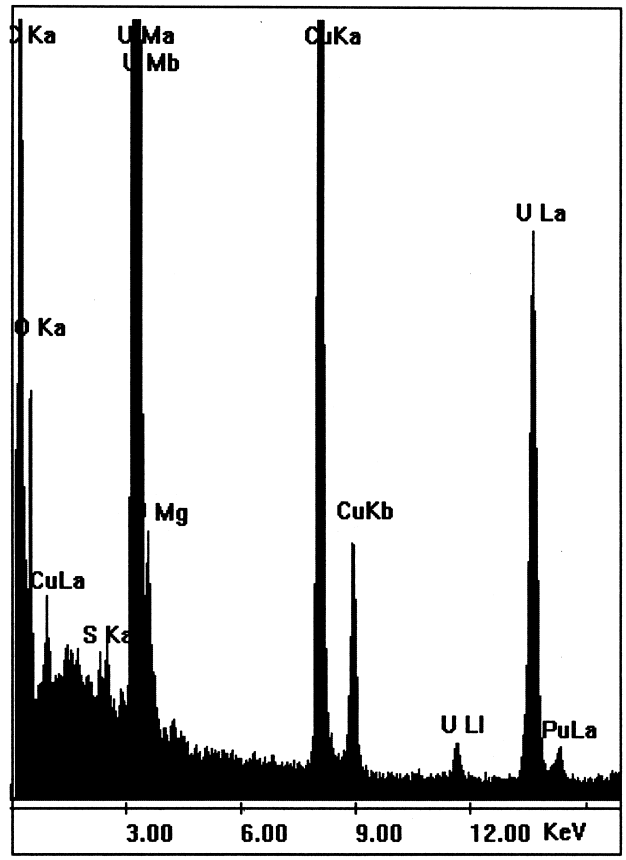

Fig. 2. X-ray spectrum on a phagocytosed MOX particle obtained by raster EDS analysis.

3. Results

The particles containing heavy elements were easily identified at low magnification within the entire cells using either bright- or dark-field observation modes. About 35% of alveolar macrophages contained particles, and the mean number of particles per loaded macrophage was one to two. At this time, 20 particles have been analysed. The actual median diameter of the particles was 0.3 μm (SD= 0.2), and no particle with a diameter of more than 1.4 μm was encountered. All the phagocytosed particles appeared as individual particles. This was confirmed by the observa-

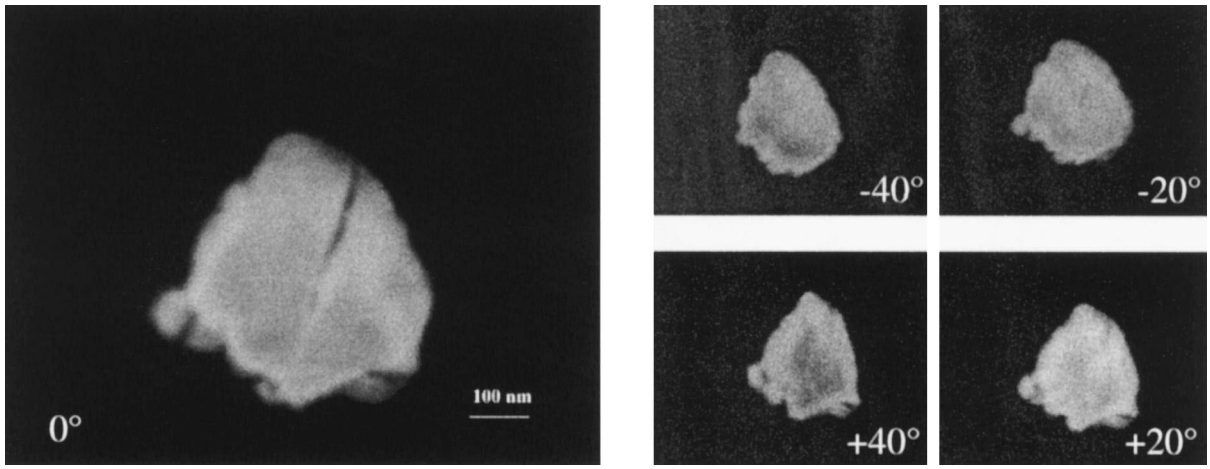

Fig. 1. Electron image of a MOX particle, made with a SOLGEL process, observed in dark-field mode (HAADF) at different tilt angles from −40 to +40°.

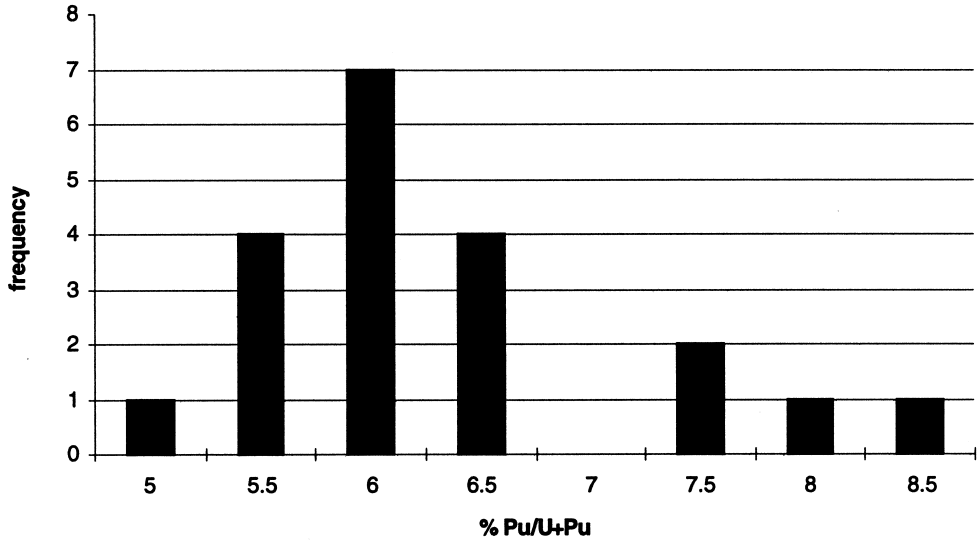

Fig. 3. Distribution of the weight ratio of Pu/U+Pu for the 20 MOX particles analysed.

tion of the same particle in dark-field mode at different tilt angles from −40 to +40° (Fig. 1).

Fig. 2 shows the spectrum of a particle obtained by raster analysis on the entire particle including the specific U and Pu Lα X-rays. In this case, the Pu/U+Pu weight ratio was 5.9%. Fig. 3 shows the distribution of the Pu/U+Pu weight ratio for each particle analysed, which varied in a range of 5–9%. The weight ratio of Pu/U+Pu was 6.6%, SD=0.9. The U and Pu element mapping shown in Fig. 4 clearly visualizes uniform distribution of Pu within the particle. Such a uniform distribution was observed for each of the 20 particles analysed, even for the largest one.

4. Discussion and conclusion

Because of the negligible amount of U and Pu in control alveolar macrophages, EDS analysis, using STEM at 200 kV performed on entire particles included within this biological matrix, appears to be a suitable method to characterize the homogeneity of the chemical composition of inhaled MOX powders, i.e. the uniform distribution of Pu within each particle. Moreover, it provides data on the mean number of particles per cell and on the shape and size of the particles [11].

This homogeneous chemical composition of MOX measured by raster EDS analysis was confirmed in the range of a few nm by Pu mapping.

The observed results demonstrate that inhalable particles obtained according to a SOLGEL process have a similar chemical composition between particles. After raster EDS analysis, all the MOX particles analysed contained measurable amounts of Pu. The weight ratio of Pu/U+Pu varied over a range from 5 to 9%, which is consistent with the global content (5.3%) determined by radiochemistry. This could not be explained by measurement uncertainty but probably was related to the SOLGEL process.

Thus, in spite of the low number of particles analyzed, we can conclude that inhalable particles obtained according to a SOLGEL process correspond to a homogeneous composition, probably a solid solution. Thus, such particles containing variable amount of Pu appear suitable as references for pulmonary toxicology study of ‘heterogeneous’ inhalable MOX particles obtained by COCA or MIMAS processes [8]. The shape of the particles seems to vary depending on the way of obtaining the inhalable particle. Thus, we have previously reported that most inhaled UO_2 particles obtained by milling were single particles [13], whereas most inhaled MOX obtained after dry grinding correspond to aggregates [9]. However, preliminary results suggest than the dissolution parameters of inhalable actinide oxides depend on the way of obtaining particles [14]. Thus, further studies are in progress for a better characterization of the physico-chemical properties of inhalable MOX particles, including their dissolution parameters after inhalation using similar homogeneous and heterogeneous MOX powders, obtained either after milling or grinding.

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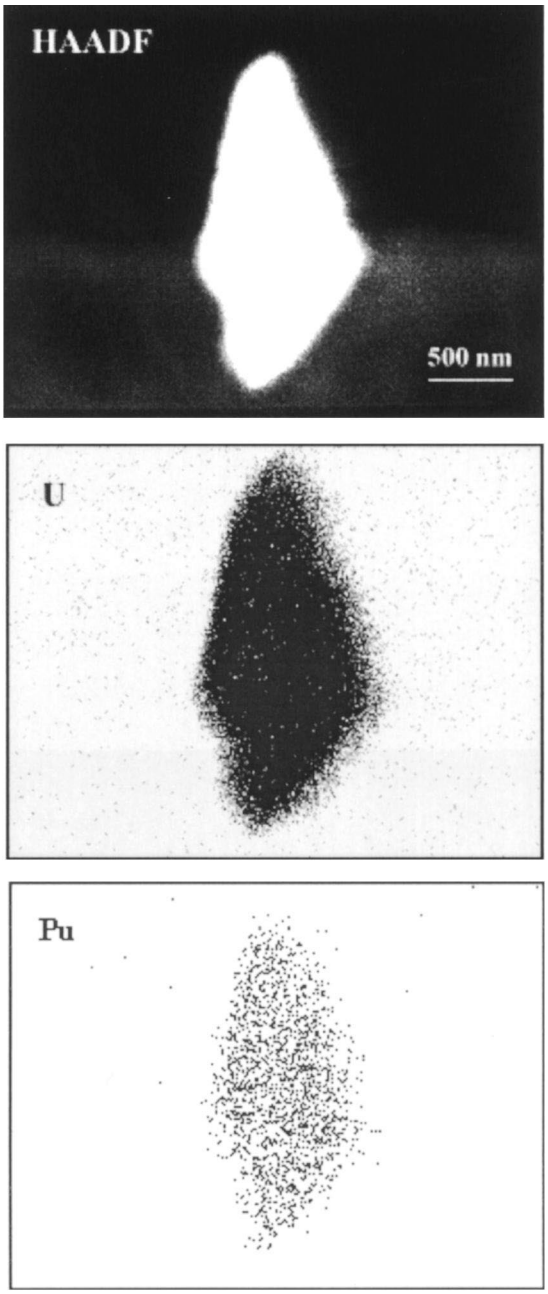

Fig. 4. Electron image using dark-field mode (HAADF) of a MOX particle and the corresponding U Lα and Pu Lα X-ray mapping.

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