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Journal of Nuclear Materials 244 (1997) 16–21

journal of nuclear materials

Transmutation of iodine: results of the EFTTRA-T1 irradiation test

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Received 9 September 1996; revised 27 November 1996

Abstract

The transmutation of the fission product iodine has been studied by irradiation tests in the High Flux Reactor at Petten. Three different metal iodides, containing natural ^{127}I, have been irradiated during eight reactor cycles (192.95 full power days): cerium iodide (CeI_3), sodium iodide (NaI) and lead iodide (PbI_2). The samples were encapsulated in 15–15 Ti stainless steel. The burn-up as well as the behaviour of the samples and cladding have been studied by post-irradiation examinations. Taking into account the physical properties and the experience from the fabrication of the targets, NaI seems to be the best target material for transmutation of iodine, although not ideal.

1. Introduction

The fission product iodine-129 contributes significantly to the long-term radiological effects of the treatment of wastes from nuclear power plants [1]. Apart from, of course, its radiotoxicity resulting from β-decay, this is due to its long half-life (1.57×10^7 year) and its high mobility in the geosphere. Presently, three relevant management modes can be considered for ^{129}I from reprocessing [2]:

- controlled discharge into the environment;
- trapping from off-gases followed by disposal in rocks or ocean, beds;
- trapping followed by transmutation.

Controlled discharge is the current practice at the reprocessing plants, which is justified by the fact that sufficient isotopic dilution with natural ^{127}I will take place during global circulation. However, there is an increasing awareness that, from an ethic point of view, it is preferred to eliminate or minimize the amount of waste in the best possible way. Transmutation seems to be a potential method to achieve this since ^{129}I can be transformed to the stable xenon isotope ^{130}Xe by a single neutron capture:

$$^{129}I + n \rightarrow {}^{130}Xe + \beta^-.$$

However, transmutation rates in existing reactor types are low whereas the required inventories are high [3,4]. Major problems also arise in finding suitable materials for the production of targets for transmutation because of the corrosive nature with respect to most technical alloys and the high volatility of elemental iodine and many of its compounds.

In the present study, irradiation tests of iodine have been performed in the High Flux Reactor (HFR) at Petten using multigram samples of three different target materials (containing ^{127}I), with the aim to study the material behaviour. To our knowledge, such an experiment had not been performed before. The transmutation experiments on iodine (^{129}I) described by Wootan et al. [5] were done in a Fast Flux Test Facility using milligram-sized samples and, moreover, served a different aim.

The present work is part of the EFTTRA cooperation [6] and preliminary results have been presented at the GLOBAL conferences [7–9].

2. Selection of target materials

The following criteria have been used for the selection of the target material:

- the metal component should have a low cross-section for thermal neutron capture;
- no long-lived isotopes should be produced during irradiation;

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PII S0022-3115(96)00729-5

- the compound should have a high iodine content;
- the compound should be thermodynamically stable at the operating temperature of power reactors (about 350 to 800°C),
- the compound should be compatible with the cladding material (very likely stainless steel because of the long irradiation times required in all existing reactor types).

It should be noted that an important additional criterium should have been the compatibility with the cooling medium of the transmutation device, but since metal iodides are in general very soluble in water (coolant of thermal reactors) and, with the exception of NaI, little is known about their solubility in liquid sodium (coolant of fast reactors), this has not been taken into consideration in this first selection.

The properties of a selection of the most promising metal iodides are summarized in Table 1 and Fig. 1 [10,11]. The materials can be classified in groups of similar properties. CeI_3 and YI_3 clearly seem the most promising materials, having a relatively low cross-section for thermal neutron capture, a reasonably high melting point, a low vapour pressure and a high thermodynamic stability. However, they present the disadvantage of being instable towards moisture and oxygen (they easily form oxy-iodides) and are hitherto difficult to prepare in a pure form. PbI_2 and ZnI_2 are least stable in terms of thermal dissociation, have the highest vapour pressure among the compounds considered, but are relatively easy to handle. Since these compounds have a relatively low melting point, they will be in a molten state at the conditions in most power reactors. MgI_2 and NaI have intermediate characteristics, and are therefore in most aspects less promising than CeI_3 or YI_3. Because NaI is much less sensitive to moisture than MgI_2, it seems to be a better candidate.

A secondary criterium for the selection of the target materials is the compatibility of the target preparation with the reprocessing technology. Liquid scrubbing as well as solid adsorbents have been suggested for the removal of iodine from the gas streams in reprocessing facilities [12]. In the case of liquid removal processes iodine is bonded in metal compounds such as NaI (caustic scrubbing), HgI_2 (Mercurex) or $Ba(IO_3)_2$ (Iodox). In case of solid adsorbents only Ag seems to be an attractive bonding agent. However, in order to reduce the costs of this adsorption process (Ag is rather expensive), conversion of AgI to PbI_2 has been suggested. Thus, PbI_2 and NaI have the advantage of being possible chemical forms in which the fission product iodine can be isolated in the PUREX reprocessing facilities.

Taking the above into consideration, the following

Table 1
Properties of some metal iodides, where σ_{metal} is the thermal cross-section of the metal component (at $E_0 = 0.0253$ eV) and N_{I} the number of iodine atoms per cm^3

Compound	σ_{metal} (b)	$N_{\mathrm{I}}/10^{-22}$ (cm^{-3})	Melting point (K)
CeI_3	0.73	1.97	1033
MgI_2	0.064	1.94	1906
YI_3	1.30	1.76	1238
NaI	0.543	1.47	934
PbI_2	0.18	1.59	683
ZnI_2	1.10	1.80	719
^{127}I	6.2	–	–
^{129}I	34	–	–

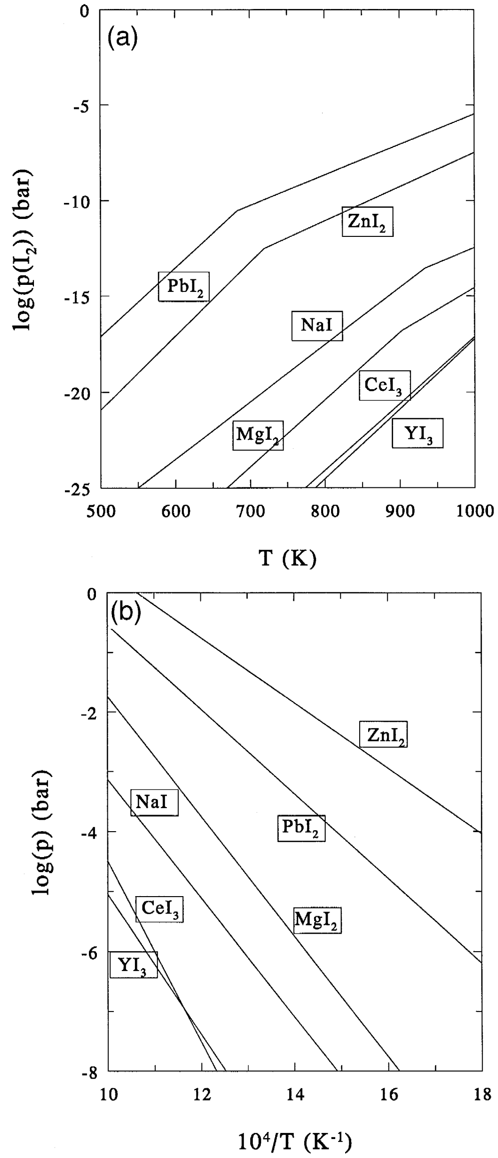

Fig. 1. The dissociation pressure log($p(I_2)$) as a function of the temperature (a) and the vapor pressure as a function of the reciprocal temperature (b) of some metal iodides.

Table 2
Chemical analysis of the materials

Compound	mass% metal		mass% iodine	
	found	calc.	found	calc.
CeI_3	26.88 ± 0.01	26.90	72.84 ± 0.02	73.10
PbI_2	44.73 ± 0.15	44.94	55.03 ± 0.18	55.06
NaI	15.36 ± 0.03	15.34	84.72 ± 0.09	84.66

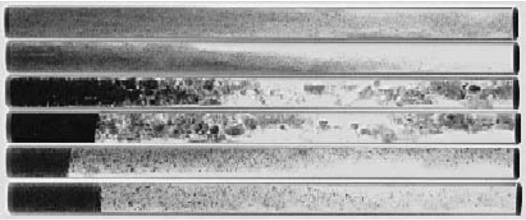

Fig. 3. X-ray photographs of the irradiated samples; from top to bottom: NaI (sample No. 1), NaI (2), PbI_2 (3), PbI_2 (4), CeI_3 (5), CeI_3 (6).

materials have been selected for the present irradiation experiments: CeI_3, PbI_2 and NaI, each representing one of the three groups mentioned earlier.

3. Target preparation and characterization

The iodine targets contained the naturally occurring isotope ^{127}I because it was not possible to prepare samples containing ^{129}I of the required quantity (1–2 g). Since the transmutation process of ^{127}I is almost identical (it is transmuted to ^{128}Xe) and since the primary goal of the irradiation is the study of the material behaviour, this was not considered to affect the meaning of the experiments.

The materials were purchased from CERAC and purified before use, after which they were stored in an argon-filled glovebox. PbI_2 and NaI were purified by heating in a stream of argon at 400 K. For CeI_3 this method could not be applied since the oxy-iodide CeOI is easily formed by reaction with adsorbed water present in the product of CERAC. Therefore this compound was purified by high-temperature sublimation. A small-scale quartz sublimator was constructed in which a removable molybdenum sample container was placed. The sample was heated at 1223 K in high vacuum ($< 10^{-4}$ Pa) and pure, bright-yellow CeI_3 deposited on a water-cooled cold-finger construction. X-ray diffraction and chemical analyses (Table 2) of the final products proved the sample to be pure. Cerium and lead were analyzed by complexometric titration with a standard EDTA solution, sodium by titration with a standard caustic solution after precipitating with nitric acid and ion-exchange with H^+, and iodine by argentometric titration with standard $AgNO_3$ solution.

The materials were encapsulated in 15–15 Ti stainless steel tubes which had an outside diameter of 6.55 mm, an inside diameter of 5.65 mm and a length of 100 mm (see Fig. 2). The bottom and top were made of the 15–15 Ti rod. Tubes and rod were provided by CEA-Cadarache. The bottom of the capsules was welded in air, but because of the highly hygroscopic character of the materials (especially CeI_3) the top had to be welded in an inert atmosphere. To this purpose a special exsiccator was designed to transfer the samples from an argon-filled glove box, in which the filling of the capsules was done, to the welding facility. The top of this exsiccator was made of planparallel quartz through which the laser beam could be guided to enable laser-welding inside. In addition, the exsiccator was equipped with a gas-flow connection and a vacuum connection. These were used to remove the argon from the exsiccator and the plenum of the tubes and substitute it with helium gas.

Before the start of the irradiation, X-ray photographs of the targets were made, as shown in Fig. 3. It is clear that the sample materials do not only occupy the bottom section of the capsule, but also adhere to the cladding due to the static character of the powders.

4. Irradiation conditions

Six targets, two of each selected material, were irradiated in the central in-core position C5 of the HFR-Petten [13] during 8 reactor cycles (192.95 full power days). Details of the irradiation device and sample holder can be found in Ref. [7].

The neutron fluence was monitored by means of gamma-scan wires and fluence detector sets. The results of the post-test analysis of the neutron fluence monitor show that the mean total neutron fluence was about 2×10^{26}

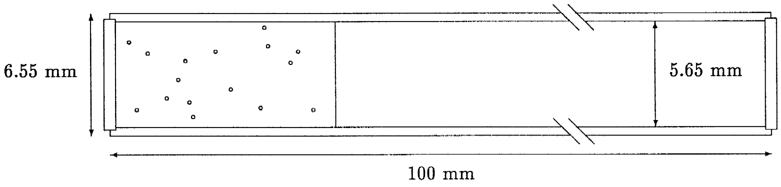

Fig. 2. The capsule for irradiation of the metal iodides; left hand part represents the sample material.

Fig. 4. X-ray photographs of the irradiated samples; from top to bottom: NaI (sample No. 1), NaI (2), PbI_2 (3), PbI_2 (4), CeI_3 (5), CeI_3 (6).

m^{-2} with a thermal component of 3.2×10^{25} m^{-2} (E,0.7 eV), a fast component of 8.8×10^{25} m^{-2} ($E > 0.1$ MeV) and an intermediate component of 7.5×10^{25} m^{-2}.

The temperature in the sample holder was measured by nine thermocouples positioned close to the samples. During the eight irradiation cycles the temperature fluctuated around 700 K, due to variations in the gamma heating, but the temperature always exceeded 679 K (the melting point of PbI_2).

5. Post-irradiation examination

During the dismantling of the facility, it became clear that the capsules containing lead iodide had swelled considerably since they could not be removed from the sample holder by standard methods. After they had been removed mechanically, a distinct blackening of the aluminium of the sample holder near one of the PbI_2 capsules indicated that leakage had occurred. Visual inspection showed a small hole in the cladding of at least one target. The deformation of the cladding could also be seen on X-ray photographs of the irradiated targets which revealed that the swelling only occurred in the bottom region where the molten salt is located (Fig. 4). We therefore concluded that the reaction between salt and cladding is most probably the cause of this effect. The X-ray photographs of the targets containing the cerium and sodium iodide samples did not show evidence for interaction between salt and cladding.

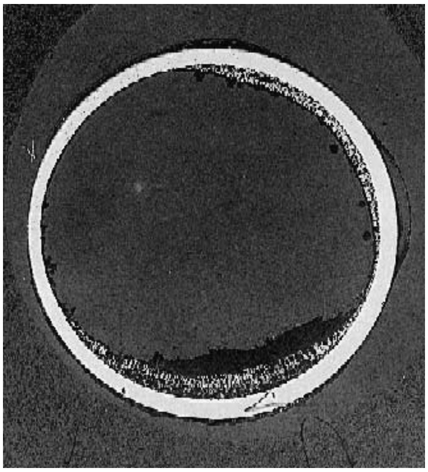

Fig. 6. Cross-section of the lead iodide capsule after irradiation.

Axial diameter measurements of the capsules confirmed the swelling of the PbI_2 capsules (Fig. 5). At 9 mm above the bottom of the capsule the diameter was 6.73 mm, compared to 6.55 mm for the unirradiated material,

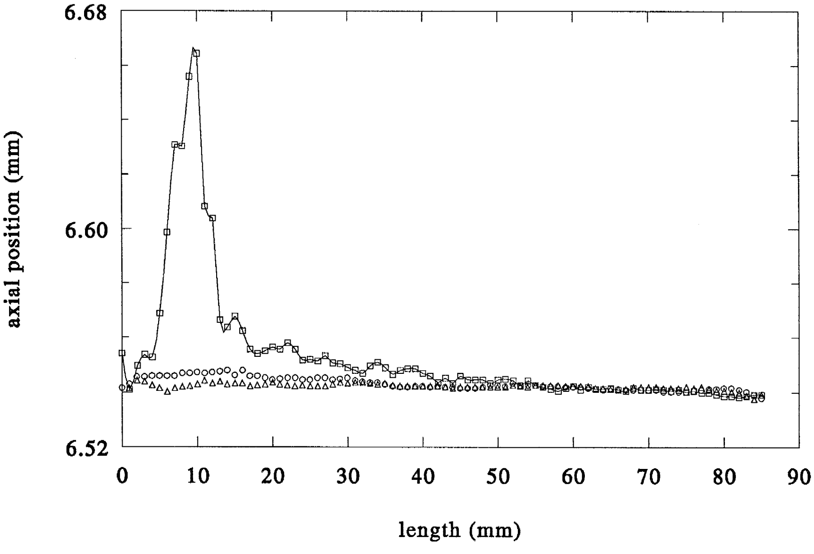

Fig. 5. Axial diameter measurements of the iodine capsules after irradiation; □, PbI_2; ○, NaI; △, CeI_3.

i.e., an increase of 2.7%. For NaI an insignificant increase of the diameter was observed in the region where the metal iodide was located.

Microscopic examination of the capsule material showed that severe attack of the inner wall of the PbI_2 capsule had occurred (Fig. 6). The wall thickness of the capsule varied from 0.367 mm to 0.214 mm, compared to 0.45 mm for the unirradiated material. Electron probe microanalysis (EPMA) of the capsule showed (a) dissolution of lead in the steel and (b) segregation of a phase containing iron, nickel, chromium as well as iodine (Fig. 7). No attack of the wall was observed for the CeI_3 and NaI capsules.

The burn-up of iodine was determined by puncturing of the capsule, followed by mass-spectrometric analysis of the plenum gas. Since the cladding of the two lead iodide

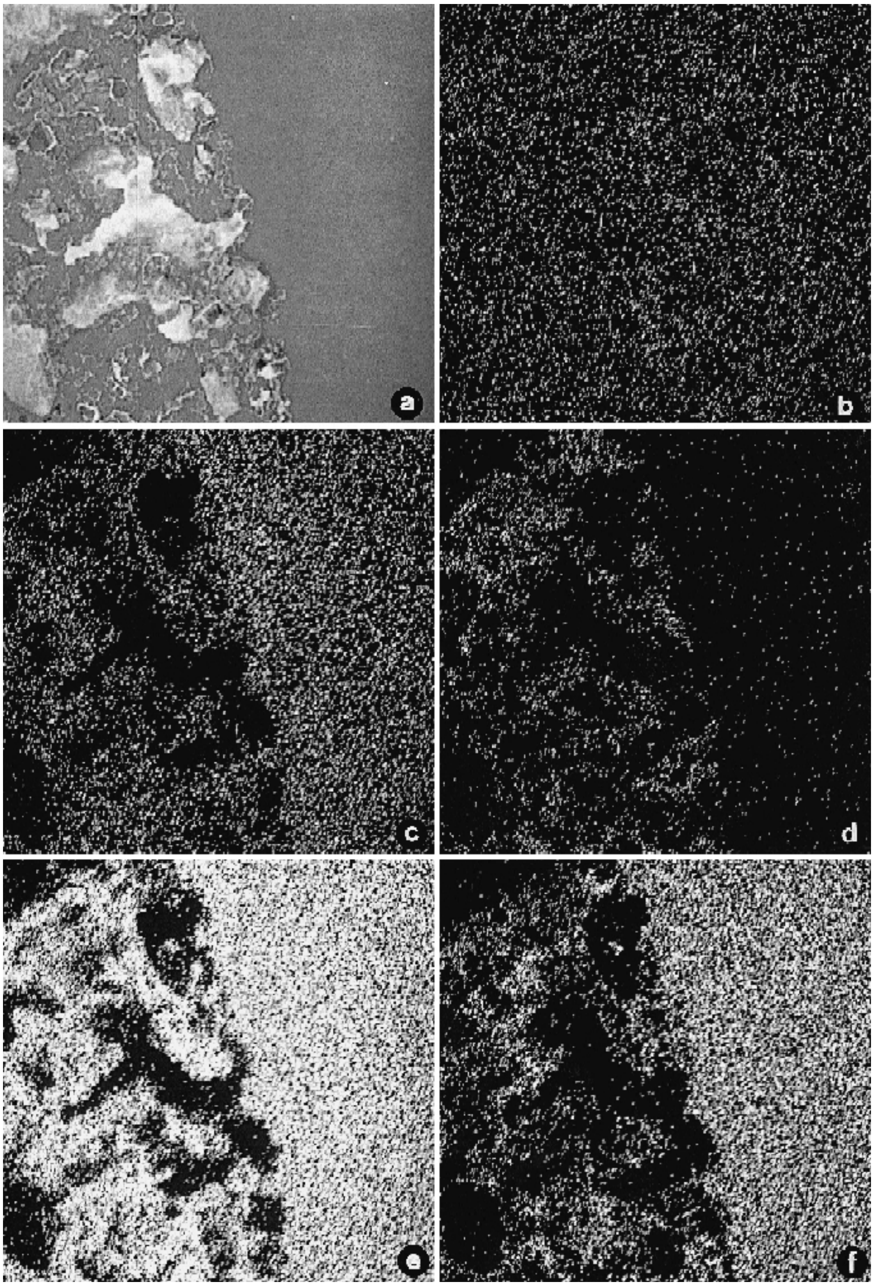

Fig. 7. Electron probe microanalysis of the capsule containing PbI_2; (a) SEM image; (b–f) distribution images of Pb, Cr, I, Fe and Ni, respectively.

Table 3
Results of the burn-up measurements for the iodine samples

Sample	Content	Isotope composition Xe (at.%)			Burn-up (at.%)
		^{128}Xe	^{129}Xe	^{130}Xe	
1	NaI	99.2405	0.7078	0.0517	5.14
2	NaI	99.2365	0.7111	0.0524	5.12
5	CeI_3	99.2247	0.7213	0.0540	5.86
6	CeI_3	99.2232	0.7238	0.0530	5.87

capsules had failed, burn-up data have only been obtained for the sodium and cerium iodide samples. The results, summarized in Table 3, show excellent agreement between the two samples of each material: the burn-up was 5.13 at.% for NaI and 5.87 at.% for CeI_3.

6. Discussion and conclusions

The results of the post-irradiation examinations show that NaI as well as CeI_3 are compatible with 15–15 Ti stainless steel, whereas PbI_2 is not. This is concordant with our pre-test analysis which showed that the thermodynamic stability of PbI_2 is much lower than that of the two other compounds. Also the fact that PbI_2 was in a molten state during irradiation probably will have enhanced the interaction as it will have resulted in an enlarged reaction surface.

Only small differences were observed in the irradiation behaviour of CeI_3 and NaI. Firstly, the cladding of the NaI capsules showed a very slight swelling in the region where the salt was located. Secondly, the measured burn-up for NaI was somewhat lower than that for CeI_3. The latter observation is most likely due to differences in the properties of the powders: the more static NaI powder adhered significantly more to the inner wall of the cladding (see Fig. 3), as a result of which part of the material was positioned in a lower neutron flux due to the axial variation along the capsules.

Apart from the irradiation behaviour, the experience gained during the fabrication process should also be considered in the recommendation of a good target material. From the description above, it is clear that the handling of CeI_3 is problematic: it reacts very easily with oxygen and water, releasing iodine in the form of I_2(g) or HI(g). This can only be avoided by careful handling in an inert atmosphere. Also, the compatibility with PUREX reprocessing technology cannot be neglected in the choice of a suitable material. As noted before, NaI, as the product of liquid scrubbing of off-gases, and PbI_2, as the product of the conversion of AgI from solid adsorbents, are possible products from iodine removal.

The overall conclusion of the present study is that if transmutation of iodine is considered, sodium iodide is the best target material, although mediocre in many aspects.

Acknowledgements

R. Belvroy, F. van den Berg, H. Buurveld and G. Dassel are acknowlegded for having performed the post-irradiation examinations; H. Gruppelaar and J.-F. Babelot are thanked for critical reading of the manuscript.

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