Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Nuclear Materials 320 (2003) 25–30

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Selection of chemical forms of iodine for transmutation of ^{129}I

Yoshiro Shirasu *, Kazuo Minato

Department of Materials Science, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan

Abstract

To select suitable chemical forms of iodine for the target for transmutation of ^{129}I, the properties of iodine compounds of NaI, MgI_2, CaI_2, CuI and $Ca(IO_3)_2$ were compared and the out-of-reactor heating experiments of the pellets of CuI and $Ca(IO_3)_2$ with the cladding materials were carried out. CuI and $Ca(IO_3)_2$ are not deliquescent but stable in the air, which is of great advantage to construction, operation and maintenance of the processing plants. The cladding with Cu metal liner could be compatible with CuI though the compatibility of the stainless steel with CuI is not good. $Ca(IO_3)_2$ should be deleted from the list of the candidate target materials for the transmutation of ^{129}I due to the severe chemical reaction with the cladding materials.

1. Introduction

The concept of partitioning and transmutation of long-lived nuclides is an attractive option to reduce the long-term risk of the storage of high-level waste from nuclear reactors. Besides the minor actinides, the long-lived fission product iodine-129 is widely recognized as one of the main fission products contributing to the radiotoxicity for a very long time. Iodine-129 decays by beta emission with a half-life of 1.57×10^7 years. The cumulative yields for ^{129}I from thermal neutron fission of ^{235}U and ^{239}Pu are 0.75% and 1.40%, respectively. About 5.54 kg/GWey of ^{129}I, together with about 1.22 kg/GWey of a stable nuclide of ^{127}I, are contained in the UO_2 spent fuel of light water reactors burnt to 60 GWd/t after 5 years cooling [1].

The transmutation of ^{129}I is accomplished by a single neutron capture, followed by rapid decay to stable ^{130}Xe. Additional neutron capture also results in other stable isotopes ^{131}Xe and ^{132}Xe. Irradiation experiments for the transmutation, together with the related experiments, have been reported in the literature [2–6]. The milligram-sized physics sample of ^{129}I was irradiated in the Fast Flux Test Facility (FFTF) by Wootan et al. [2]. The EFTTRA-T1 experiment was performed by Konings, where multi-gram powders of NaI, CeI_3 and PbI_2 were irradiated in the High Flux Reactor (HFR) as candidate target materials [3]. The pellets of MgI_2, CaI_2, CuI and NaI were irradiated in HFR in the Project I irradiation by Schram et al. [5]. In the last two irradiation tests, natural iodine, ^{127}I, was used instead of ^{129}I, since the transmutation process of ^{127}I is almost identical to that of ^{129}I. In the framework of the OMEGA program in Japan, JAERI has started literature survey and experimental studies concerning transmutation of ^{129}I [6]. Although these studies were performed, the argument about chemical forms of the target materials has not been concluded.

In the present study, properties of iodine compounds were compared with one another again from the viewpoint of the target materials for the transmutation of ^{129}I, and out-of-reactor heating experiments of candidate target materials were carried out to select suitable chemical forms of the target.

2. Properties of iodine compounds

Elemental iodine, I_2, is not a suitable chemical form of the target for the transmutation of ^{129}I since its melting point of 386.8 K and boiling point of 457.7 K are low and it is very corrosive. Some attempts have

---

[*] Corresponding author. Tel.: +81-29 282 5402; fax: +81-29 282 6442.

E-mail address: shirasu@analchem.tokai.jaeri.go.jp (Y. Shirasu).

0022-3115/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-3115(03)00164-8

been made to select suitable chemical forms of the target through the literature survey and the irradiation tests [3–6]. The criteria for the selection of chemical forms of the target used in the previous studies were the melting point, the melting point of the metal component, the thermal neutron capture cross section of the metal component, the production of no long-lived nuclide, the content of iodine, the compatibility with the cladding materials, the chemical stability in the air, etc. Unfortunately, no compound was found to fulfill the criteria.

The EFTTRA-T1 experiment revealed that NaI was the best target material among NaI, CeI_3 and PbI_2 [3]. The Project I irradiation showed that CuI was a less suitable compound in view of the compatibility with the steel [5]. On the other hand, it was pointed out that CuI is stable in the air, which is very favorable for fabrication and handling of the target [6].

Table 1 compares the properties of the candidate compounds for the transmutation of ^{129}I. The compounds listed in the table were selected ones in the above three studies [3,4,6]. In the case of NaI and MgI_2, no long-lived nuclide will be produced, but they are deliquescent. When CaI_2 and $Ca(IO_3)_2$ are used, long-lived nuclide ^{41}Ca ($T_{1/2} = 1.03 \times 10^5$ y) is produced by a single neutron capture of ^{40}Ca though the total radiotoxicity decreases. The reduction behavior of the radiotoxicity was discussed as a function of time in the previous papers [6,7]. CuI and $Ca(IO_3)_2$ are not deliquescent but stable in the air. This means that no special atmosphere control is needed for handling, which is of great advantage to construction, operation and maintenance of the processing plants.

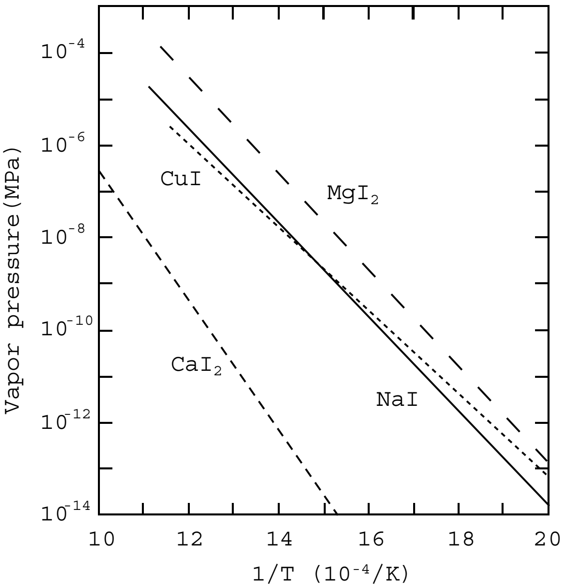

Fig. 1. Vapor pressures over solid NaI, MgI_2, CaI_2 and CuI as a function of inverse temperature.

Fig. 1 shows the vapor pressures over solid NaI, MgI_2, CaI_2 and CuI, respectively, which were calculated on the basis of the thermodynamic data [8,9]. The vapor pressure is one of the factors relating to the transport of the materials. Among these compounds, MgI_2 has the highest vapor pressure and CaI_2 has the lowest one. The main gaseous spices over NaI, MgI_2 and CaI_2 are iodides of NaI(g), Na_2I_2(g), MgI_2(g) and CaI_2(g), respectively, while those over CuI are I(g) and I_2(g), as shown in Fig. 2. This difference may influence the chemical interaction with the cladding materials. The gaseous I(g) and I_2(g) transferred from CuI could interact with the cladding materials.

For the compatibility with the cladding materials, the neutrongraphs suggested chemical interaction between CuI and the steel end plugs in the Project I irradiation [5]. Fig. 3 shows the relative partial molar Gibbs free energies of iodine of the metal iodides as a function of temperature, which were taken from the databases [9,10]. The elements of Fe, Ni, Cr, Mo and Mn are the main components of the candidate cladding materials of 316-stainless steel and 2.25Cr–1Mo steel. With this figure the chemical interactions could be predicted thermodynamically. This figure indicates that CuI interacts with Cr and Mn to form CrI_2 and MnI_2 thermodynamically, while NaI, MgI_2 and CaI_2 do not react with Fe, Ni and Cr that are the components of the stainless steel. Taking these things into consideration, a new idea is needed concerning the compatibility with the cladding materials when CuI is used as the target material.

Table 1
Properties of iodine compounds

Compound	Melting point (K)	Melting point of metal (K)	Number density of I-atoms (10^{22}/cm^3)	Production of long-lived nuclide: half-life	Chemical stability
NaI	933	370.98	1.47	No	Deliquescent
MgI_2	907	922	1.84	No	Deliquescent
CaI_2	1052	1112	1.62	^{41}Ca: 1.03×10^5y	Deliquescent, light sensitive
CuI	868	1358	1.78	^{65}Zn: 244.26 d, ^{63}Ni: 100.1 y	Stable in the air
$Ca(IO_3)_2$	823 (dcm)[a]	–	1.40	^{41}Ca: 1.03×10^5y	Stable in the air

[a] Decomposition.

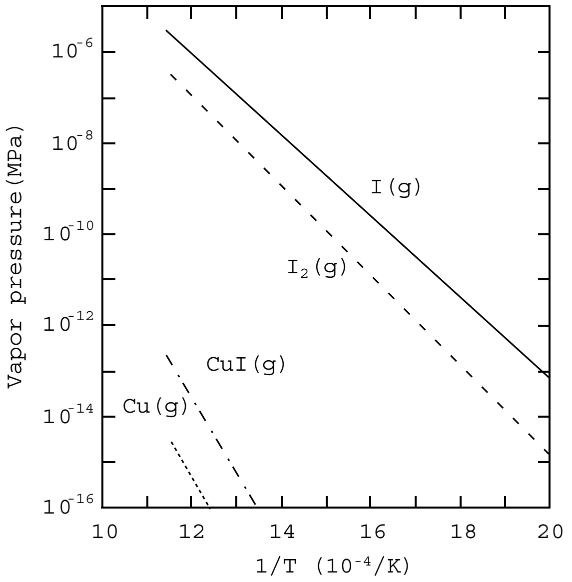

Fig. 2. Partial pressures of I(g), I_2(g), CuI(g) and Cu(g) over solid CuI as a function of inverse temperature.

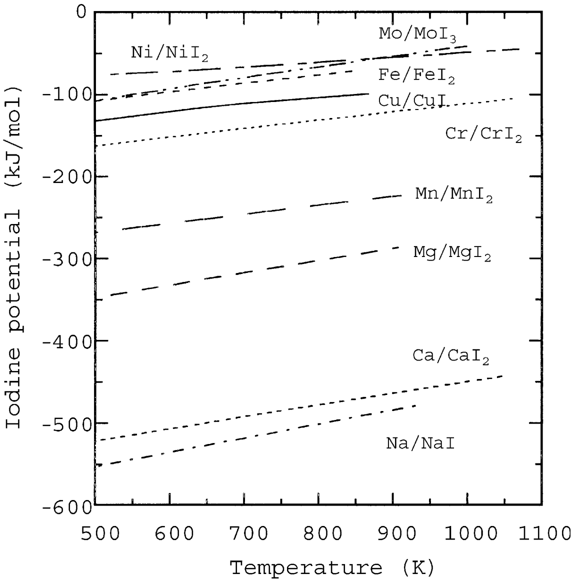

Fig. 3. Relative partial molar Gibbs free energies of iodine of the metal iodides as a function of temperature.

3. Heating experiments

3.1. Samples and procedure

As CuI and $Ca(IO_3)_2$ have a good chemical stability in the air, out-of-reactor heating experiments of CuI and $Ca(IO_3)_2$ with cladding materials were carried out to clarify whether they are valid candidate target materials for the transmutation of ^{129}I or not. The commercial powders of CuI and $Ca(IO_3)_2$ with a stable isotope ^{127}I were used in the present experiments. The X-ray diffraction analysis on the as-received CuI (>99.99%) revealed no second phase, while that on the as-received $Ca(IO_3)_2$(>99%) revealed that it contained crystal water.

For the heating experiments with the cladding materials, pellet samples were prepared. The powder was pressed into pellets of about 4.4 mm in diameter and 2.5 mm in thickness at room temperature. The density of the as-pressed pellets of CuI was about 86% of the theoretical density (TD). Fig. 4 shows an as-pressed pellet of CuI. For $Ca(IO_3)_2$, the as-pressed pellets were thermally treated at 573 K for three hours in flowing argon to dehydrate them. The density of the $Ca(IO_3)_2$ pellets after the heat-treatment was about 71%TD.

The pellets of CuI and $Ca(IO_3)_2$ were sandwiched by the metal plates of 316-stainless steel, 2.25Cr–1Mo steel, or Cu, which were sealed one by one in quarts tubes filled with purified helium. The dimensions of the plates were 5, 6 and 1 mm. The tubes containing the samples were heated in an electronic furnace. The experimental conditions are summarized in Table 2.

3.2. Results and discussion

The pellets of CuI were heated with the plates of 316-stainless steel and 2.25Cr–1Mo steel. Figs. 5 and 6 show the plates after heating at 723 K for 100 h. The contacted parts with the pellets of CuI could be recognized in both the cases. The part of the surface of the 316-stainless steel plate was discolored, indicating the slight corrosion. In the case of the 2.25Cr–1Mo steel plate, the central part of the surface was rough and discolored. Corrosion of the plates was also observed. As CuI will not interact with Fe, Ni and Mo thermodynamically, the corrosion must have caused by the reactions of CuI with Cr and Mn as well as those of I(g) and I_2(g) with Fe, Ni, Mo, Cr and Mn, as shown in Fig. 3. On the surfaces of both the plates, a large number of small particles were observed that were considered to be Cu metal; the

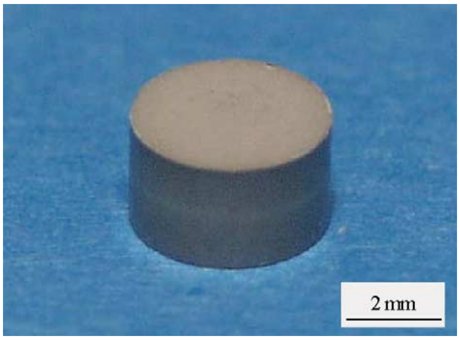

Fig. 4. As-pressed pellet of CuI.

Table 2
Experimental conditions of heating tests

Sample		Heating conditions		Remarks
Compound	Metal plate	Temperature (K)	Time (h)	
CuI	316-stainless steel	723	100	Slight corrosion
CuI	2.25Cr–1Mo steel	723	100	Moderate corrosion
CuI	Cu	723	100	No corrosion
CuI	Cu	723	500	No corrosion
CuI	Cu	673	500	No corrosion
$Ca(IO_3)_2$	316-stainless steel	723	100	Moderate corrosion
$Ca(IO_3)_2$	2.25Cr–1Mo steel	723	100	Severe corrosion

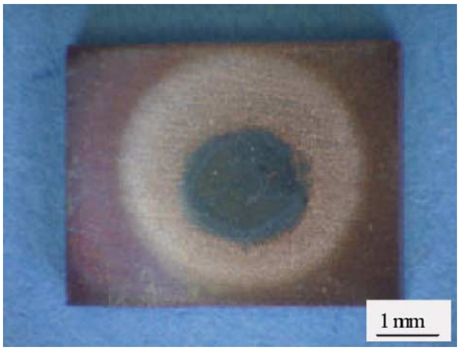

Fig. 5. 316-stainless steel plate heated with CuI pellet at 723 K for 100 h.

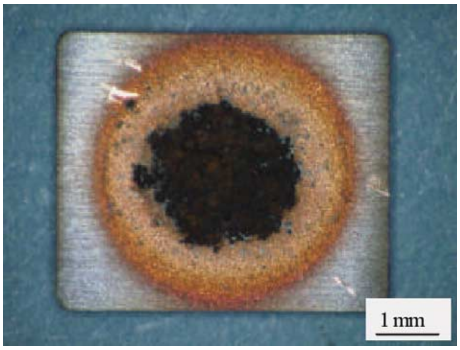

Fig. 6. 2.25Cr–1Mo steel plate heated with CuI pellet at 723 K for 100 h.

presence of Cu was detected by electron probe microanalysis.

Many small particles of this kind were also observed on the cylindrical surfaces of the pellets. An X-ray diffraction analysis revealed that these particles were Cu metal. The vaporization of gaseous I(g) and I_2(g) from CuI must have resulted in the formation of the small particles of Cu metal, as indicated in Fig. 2.

To survey the cladding materials for CuI without the corrosion, the heating experiments of the CuI pellets with the Cu plates were performed at 673 and 723 K for at most 500 h. No corrosion of the plates was observed though the particles of Cu were accumulated on the surface circularly, as shown in Fig. 7.

For the CuI pellets, the surfaces contacted with the Cu plates appeared to be almost the same as those of the as-pressed pellets, while the cylindrical surfaces showed a remarkable change. Fig. 8 shows the CuI pellet heated with the Cu plates at 673 K for 500 h. The vaporization and transportation of I(g) and I_2(g) from the cylindrical surface of the CuI pellet must have caused the change. The thermal stability of CuI is not so good. In the present experiments, the quarts tube, in which the pellet sandwiched by the plates was sealed, was more than 300 mm long and was placed along the temperature gradient of the furnace from the sample temperature down to less than the melting point of iodine, 386.8 K. Condensation of iodine was observed on the inner surface of the tube at low temperatures. This experimental configuration probably accelerated the mass transport of iodine through the vaporization and condensation mechanism.

The result of the heating experiments of the CuI pellets with the Cu plates suggested that the cladding with Cu metal liner should be compatible with CuI. The Cu metal liner has to be gastight and no cladding material, including end caps, has to be exposed. In this configuration, the structural material of the cladding can be selected regardless of the compatibility with the compounds of the target. The claddings with a metal liner are used in the fuel rods of the light water reactors; the claddings of Zry-2 with Zr metal liner are in use and the claddings of Zry-2 with Cu metal liner were tested for boiling water reactors (BWR) [11].

For the heating experiments of the $Ca(IO_3)_2$ pellets with the plates of 316-stainless steel and 2.25Cr–1Mo steel, no good result was obtained. The severe interaction was observed. Although the reaction products were not identified, oxygen must have participated in the reaction. $Ca(IO_3)_2$ has oxygen and decomposes with the release of oxygen [6].

Besides the compatibility with the cladding materials, it is very important to know the irradiation behavior and

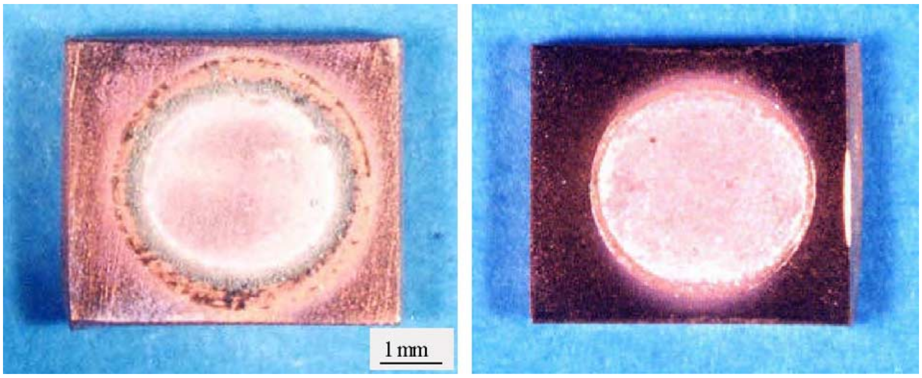

Fig. 7. Cu plates heated with CuI pellets at 673 K for 500 h (left) and at 723 K for 100 h (right).

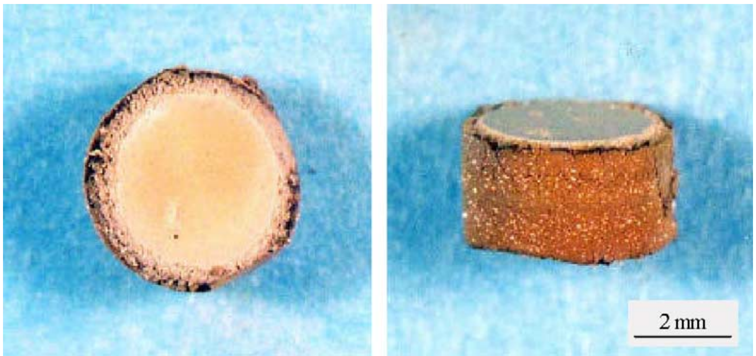

Fig. 8. CuI pellet heated with Cu plate at 673 K for 500 h.

Xe gas release behavior of the targets. And furthermore, the recycle technologies should be developed of the iodine recovery from the $AgNO_3$-impregnated silica on which iodine is adsorbed in the reprocessing plants [12], the target fabrication in a suitable chemical form for irradiation, and the re-fabrication of the targets after irradiation.

4. Conclusions

To select suitable chemical forms of iodine for the target for transmutation of ^{129}I, the properties of iodine compounds of NaI, MgI_2, CaI_2, CuI and $Ca(IO_3)_2$ were compared and the out-of-reactor heating experiments of the pellets of CuI and $Ca(IO_3)_2$ with the cladding materials were carried out. The following was concluded:

(1) CuI and $Ca(IO_3)_2$ are not deliquescent but stable in the air. This property requires no specially controlled atmosphere to handle these compounds, which is of great advantage to construction, operation and maintenance of the processing plants.
(2) The cladding with Cu metal liner could be compatible with CuI though the compatibility of the stainless steel with CuI is not good. In this configuration, the structural material of the cladding can be selected regardless of the compatibility with the compounds of the target.
(3) $Ca(IO_3)_2$ should be deleted from the list of the candidate target materials for the transmutation of ^{129}I due to the severe chemical reaction with the cladding materials.

Acknowledgement

The authors wish to express their thanks to Dr T. Ogawa, JAERI, for his interest and encouragement.

References

[1] Y. Ando, H. Takano, Estimation of LWR Spent Fuel Composition, Japan Atomic Energy Research Institute Report JAERI-Research 99-004, 1999.

[2] D.W. Wootan, D.P. Jordheim, W.Y. Matsumoto, Trans. Am. Nucl. Soc. 64 (1991) 125.

[3] R.J.M. Konings, J. Nucl. Mater. 244 (1997) 16.

[4] A. Conti, J.-P. Ottaviani, R.J.M. Konings, R.P.C. Schram, in: Proc. GLOBAL '99, Jackson Hole, USA, August 29–September 3, 1999, CD-ROM, 1999.

[5] R.P.C. Schram, K. Bakker, R. Conrad, E. Ichimura, M. Yoshizoe, in: Proc. GLOBAL 2001, Paris, France, 9–13 September 2001, CD-ROM, 2001.

[6] K. Minato, Y. Shirasu, in: Proc. GLOBAL 2001, Paris, France, 9–13 September 2001, CD-ROM, 2001.

[7] K. Nishihara, H. Takano, K. Minato, H. Oigawa, in: Proc. GLOBAL 2001, Paris, France, 9–13 September 2001, CD-ROM, 2001.

[8] E.H.P. Cordfunke, R.J.M. Konings, Thermochemical Data for Reactor Materials and Fission Products, Elsevier, Amsterdam, 1990.

[9] I. Ansara, B. Sundman, in: P.S. Glaeser (Ed.), Computer Handling and Dissemination of Data, Elsevier, Amsterdam, 1987, p. 154.

[10] I. Barin, Thermochemical Data of Pure Substances, 3rd Ed., VCH, Weinheim, 1995.

[11] K. Inoue, N. Oi, H. Maki, T. Kawada, in: Proc. ANS Topical Meeting on Light Water Reactor Fuel Performance, Orlando, USA, 21–24 April 1985, vol. 1, 1985, p. 17.

[12] G. Modolo, R. Odoj, Nucl. Technol. 117 (1997) 80.