Annals of Nuclear Energy xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Annals of Nuclear Energy

journal homepage: www.elsevier.com/locate/anucene

Experimental and modelling studies of iodine oxide formation and aerosol behaviour relevant to nuclear reactor accidents

S. Dickinson [a,*], A. Auvinen [b], Y. Ammar [c], L. Bosland [d], B. Clément [d], F. Funke [e], G. Glowa [f], T. Kärkelä [b], D.A. Powers [g], S. Tietze [h], G. Weber [i], S. Zhang [d]

[a] National Nuclear Laboratory, Building 168, Harwell Oxford Science Campus, Didcot OX11 OQT, UK
[b] VTT Technical Research Centre of Finland, Biologinkuja 7, Espoo, P.O. Box 1000, FI-02044 VTT, Finland
[c] School of Mechanical and Systems Engineering, Newcastle University, Stephenson Building, Claremont Road, NE1 7RU, UK
[d] IRSN, Cadarache, Bat. 702, 13115 Saint Paul Lez Durance Cedex, France
[e] AREVA GmbH, Dept. Radiation Protection, P.O. Box 1109, 91001 Erlangen, Germany
[f] AECL, Chalk River Laboratories, Chalk River, Ontario K0J 1J0, Canada
[g] Advanced Nuclear Energy Programs, Mail Stop 0736, Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185, USA
[h] Nuclear Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, Kemivägen 10, 41296 Göteborg, Sweden
[i] Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH, Forschungszentrum, Boltzmannstraße 14, D-85748 Garching b. München, Germany

ARTICLE INFO

Article history:
Received 3 January 2014
Accepted 6 May 2014
Available online xxxx

Keywords:
Iodine
Severe accident
Radiation
Methyl iodine
Iodine oxide
Aerosol

ABSTRACT

Plant assessments have shown that iodine contributes significantly to the source term for a range of accident scenarios. Iodine has a complex chemistry that determines its chemical form and, consequently, its volatility in the containment. If volatile iodine species are formed by reactions in the containment, they will be subject to radiolytic reactions in the atmosphere, resulting in the conversion of the gaseous species into involatile iodine oxides, which may deposit on surfaces or re-dissolve in water pools. The concentration of airborne iodine in the containment will, therefore, be determined by the balance between the reactions contributing to the formation and destruction of volatile species, as well as by the physico-chemical properties of the iodine oxide aerosols which will influence their longevity in the atmosphere.

This paper summarises the work that has been done in the framework of the EC SARNET (Severe Accident Research Network) to develop a greater understanding of the reactions of gaseous iodine species in irradiated air/steam atmospheres, and the nature and behaviour of the reaction products. This work has mainly been focussed on investigating the nature and behaviour of iodine oxide aerosols, but earlier work by members of the SARNET group on gaseous reaction rates is also discussed to place the more recent work into context.

1. Introduction

Inability to cool fuel in a Light Water Reactor (LWR) due to loss of coolant, loss of heat sink or the inability to supply coolant will lead eventually to heating of the reactor fuel, fuel cladding rupture and release of fission products. These fission products can migrate through the reactor coolant system (RCS) into the reactor containment and perhaps leak into the environment where they pose a threat to the public health and safety.

Plant assessments have shown that iodine contributes significantly to the source term for a range of accident scenarios. Iodine is a radiologically important fission product because it is biologically active and can exist in gaseous forms such as I_2 and volatile organic iodides. Although iodine would initially be released from the RCS mainly in the form of aerosols, these will be removed from the containment atmosphere by natural deposition processes and/or engineered safety systems such as sprays. After about 24 hours, the production of volatile iodine species by radiation chemical reactions occurring in water volumes or on surfaces will dominate the airborne iodine inventory in the containment, which is available for release to the environment through containment leakage or breach (along with the noble gases Kr and Xe, which dominate

Abbreviations: AECL, Atomic Energy of Canada Ltd.; BIP, Behaviour of Iodine Programme; CFD, Computational Fluid Dynamics; EDX, Energy Dispersive X-ray; LWR, Light Water Reactor; RCS, reactor coolant system; SARNET, Severe Accident Research Network; STEM, Source Term Evaluation and Mitigation; THAI, Thermal hydraulics, Hydrogen, Aerosols, Iodine; XPS, X-ray Photoelectron Spectroscopy.

* Corresponding author. Tel.: +44 7894598707.
E-mail address: shirley.dickinson@nnl.co.uk (S. Dickinson).

http://dx.doi.org/10.1016/j.anucene.2014.05.012
0306-4549/

the total airborne activity at nearly all times). It is important to understand, and be able to predict, the chemical processes that determine the behaviour of iodine in a reactor fault in order to determine with confidence if the extent and consequences of release are in line with regulatory requirements.

Iodine has a complex chemistry that determines its chemical form and, consequently, its volatility in the containment. In reducing conditions, iodine would be released from the fuel predominantly as CsI or other metal iodides, which are involatile at containment temperatures and would normally dissolve in blowdown or reflood water. Radiolytic oxidation is the main mechanism for oxidation of iodide in solution to volatile forms such as I_2. I_2 can react with surfaces in the containment, leading to its retention but also to the potential formation of volatile organic forms. Once these species are released into the containment atmosphere they will be subject to radiolytic reactions, resulting in the conversion of the gaseous species into involatile iodine oxides, which may deposit on surfaces or re-dissolve in water pools. The concentrations of volatile species in the atmosphere will, therefore, be determined by the balance between their formation and destruction reactions.

This paper summarises the work that has been done in the framework of the EC SARNET (Severe Accident Research Network) (Dorsselaere et al., 2011) to develop a greater understanding of the reactions of gaseous iodine species in irradiated air/steam atmospheres, and the nature and behaviour of the reaction products. This work has mainly been focussed on investigating the nature and behaviour of iodine oxide aerosols, but earlier work by members of the SARNET group on gaseous reaction rates is first discussed to place the more recent work into context.

2. Radiolytic oxidation of gaseous iodine species

Earlier studies of the radiolytic oxidation of gaseous iodine were mainly focussed on measuring the rates of conversion of gaseous to solid oxide products. Funke (2000) reported measurements of I_2 destruction by air radiolysis in air and steam/air atmospheres, at temperatures up to 130 °C. In these tests, which used high I_2 concentrations relative to those expected in a reactor containment, the rate of decomposition was initially zero order, although a steady-state concentration of iodine in the gas phase was reached after extended irradiation. The zero order decomposition suggests that the rate is limited by the formation of a reactive species in the irradiated air/steam atmosphere. The effect of temperature on the decomposition rate was small, and there was no significant effect of dose rate or steam concentration. The iodine radiolysis products were concluded to be I_4O_9 at 25 and 80 °C, and I_2O_5 at 130 °C.

The radiolytic oxidation of I_2 at lower initial concentrations was studied in the PARIS programme (Bosland et al., 2008, 2011). The decomposition rates in the PARIS tests do not appear to be consistent with the zero order behaviour observed in the earlier study of Funke (2000), suggesting a possible shift towards first-order decomposition kinetics at the lower I_2 concentrations.

The radiolytic decomposition of gaseous CH_3I in air was measured by Tang and Castleman (1970). They found that the decomposition was zero order at high concentrations but pseudo-first order in the range of interest here. Baston et al. (2003) measured similar decomposition rates for gaseous methyl and ethyl iodide in moist air and found no significant effect of increasing the temperature to 80 °C; increasing the water vapour concentration and the surface/volume ratio of the reaction vessel decreased the decomposition rate slightly. Decreasing the O_2 concentration of the atmosphere to 1% significantly increased the decomposition rate. In recent tests carried out as part of the OECD Behaviour of Iodine (BIP) Programme (Glowa and Moore, 2012) multiple injections of CH_3I were made into the same irradiated air volume over a period of 24 h, and this showed that the decomposition rate was not changed significantly by the build-up of irradiation products.

3. Iodine oxide aerosols: characteristics and behaviour

3.1. Gamma irradiation of I_2 vapour in air

Researchers at AECL's Chalk River Laboratories have performed gamma irradiations of I_2 vapour in air to investigate the products of this reaction at dose rates consistent with post accident containment (~0.4 to 1.8 kGy/h) (Glowa and Ball, 2012). After a few days of irradiation, a light coloured deposit was observed on the glass irradiation vessel. At high magnification (Fig. 1), it can be seen that this deposit is made up of small particles on the order of 0.5 μm in diameter. Information from Energy Dispersive X-ray (EDX) Spectroscopy is consistent with particles that are comprised of iodine and oxygen. The O to I ratio, calculated from several EDX spectra, ranges from 2.6 to 7. X-ray Photoelectron Spectroscopy (XPS) showed that iodine was present in two distinct oxidations states. These findings are consistent with a number of potential products, such as I_2O_4, I_2O_5, I_4O_9 and HIO_3.

In experiments where liquid water was present, and the relative humidity was very high, the deposit was not observed. Instead, droplets of water were observed on the horizontal surfaces, which is indicative of the hygroscopic nature of the products.

3.2. Gaseous iodine oxidation by ozone or UV irradiation

3.2.1. Large-scale tests (THAI)

The technical-scale THAI test facility (THAI = Thermal hydraulics, Hydrogen, Aerosols, Iodine) is operated by Becker Technologies at Eschborn, Germany, in close co-operation with AREVA NP and GRS in order to provide an experimental data base for the development and validation of lumped-parameter and Computational Fluid Dynamics (CFD) containment codes. One focus of THAI is the investigation of coupled containment phenomena between the areas of Thermal hydraulics, Hydrogen, Iodine and Aerosols. A full description of the facility is given elsewhere (Funke et al., 2012).

Two of the tests carried out in the facility, Iod-13 and Iod-14, studied the formation and behaviour of IO_x aerosol produced by the reaction of gaseous I_2 with ozone. The atmospheric temperature in the tests was about 100 °C and the relative humidity 60–70%.

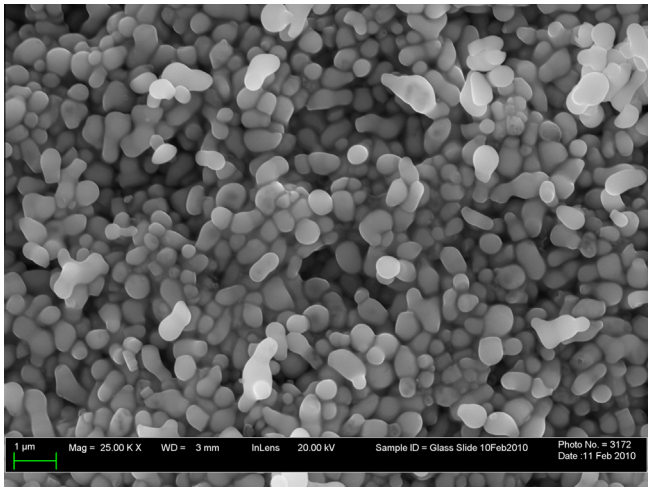

Fig. 1. SEM image of aerosol deposit from gamma irradiation of I_2 in air.

Please cite this article in press as: Dickinson, S., et al. Experimental and modelling studies of iodine oxide formation and aerosol behaviour relevant to nuclear reactor accidents. Ann. Nucl. Energy (2014), http://dx.doi.org/10.1016/j.anucene.2014.05.012