Radiochemical studies of the retention of volatile iodine in aqueous solutions

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Volatile molecular iodine and organic iodine species would be generated under radiation in the gas space and sump of nuclear power plant containments during a severe accident involving core melt. Engineered and currently installed safety systems might not effectively retain highly volatile iodine species. Fast and efficient conversion to non-volatile species within the containment would lower the potential risk of a significant release into the environment and therefore, methods must be sought to reduce iodine volatility to a minimum or, ideally, to remove it completely. This paper presents the results of an experimental programme to obtain a fast and efficient reduction of highly volatile organic iodide species in aqueous solution into iodide ions.

Introduction

Gaseous radioactive iodine, especially the ^{131}I isotope, poses a health hazard due to its easy and almost irreversible transport to the human thyroid gland, where it can locally induce cancer. During a severe accident in a nuclear power plant, a core melt may cause release of gaseous radioactive iodine into the environment. Iodine released from a degraded core and transported into the containment atmosphere undergoes complex chemical reactions in the containment atmosphere and sump water, since iodine can exist in several oxidation states (–1 to +7). The prevailing conditions, i.e., concentrations of iodine species, pH, redox potential, dose rate, temperature, and the presence of other fission products and structural materials, will determine the iodine speciation, and the extent of their reactions in the sump water as well as in the containment atmosphere.

Organic iodides are generated by the reactions of molecular or iodine radicals with wall paint in the containment atmosphere¹ or with organic radicals in sump water under irradiation. The latter are products of thermal or radiolytic destruction of organic materials, such as cables and oils, etc. Although some of the main routes for organic iodine production have been identified, there are uncertainties regarding the reactions of organic materials in containments under radiation and heat, and their reactions with iodine species. In addition, large variations in the boundary conditions, which are specific to the design and operation of the NPP, such as different paints and presence of other organic materials make a reliable estimate of organic iodide generation very difficult. Depending on the sump water volume, and the amount of destroyed organic materials, iodine generation can be more significant here than in the containment atmosphere. However, due to the very low partition coefficients, coupled with the high volatility of some organic iodines in the sump water, a potential risk for the accumulation of airborne iodine species exists.

Concurrent to organic iodide formation in redox reactions, especially under irradiation, it can decompose to form radicals, molecular iodine, iodide or iodine oxides by hydrolysis and radiolysis. Decomposition will also take place in the gas phase as a consequence of the presence of airborne oxidizing species (O_3 , NO_2 , etc.).

However, experimental programmes have confirmed the existence of gaseous organic iodine, in some cases in higher concentrations than for molecular iodine.¹ Methyl iodide (CH_3I) is the most volatile member of the organic iodine group. Its reaction with surfaces is slower, and its removal by engineered systems, e.g., by containment filters and scrubbers, is less efficient in comparison with molecular iodine. Therefore, low destruction rates introduce a large uncertainty for occurrence of a high iodine source term even with the implemented engineered safety systems.

Experimental programme

The main aim of the PSI investigations is to seek chemical reagents (additives), which will efficiently and rapidly decompose volatile organic iodides in the sump and to establish a sound database for the destruction rates. The database can then be used for devising strategies for accident management aimed at retaining iodine in the reactor containment. An experimental programme in three consecutive stages was conducted:

(1) Experiments providing decomposition by hydrolysis only at certain conditions relevant to our programme and in view of the rather scattered data available in the literature.

(2) Experiments studying CH_3I decomposition by radiolysis at two reference temperatures.

(3) Experiments producing a comprehensive database for the effect of selected additives.

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Experimental facility

A special facility (Fig. 1) was developed enabling irradiation of the aqueous iodine (methyl iodide and cesium iodide) using in-situ β -irradiation or external irradiation using a γ -source. Additionally, special techniques were developed to prepare tagged methyl iodide solutions and for a fast and easy determination of the main species of iodine² (Fig. 1) in the samples taken from the gas and aqueous phases of the facility.

Synthesis of $\text{CH}_3^{131}\text{I}$ and preparation of CH_3I aqueous solutions

A concentrated and tagged methyl iodide solution was prepared either by methylation of an aqueous solution of labeled potassium iodide (KI) or by isotopic exchange between liquid methyl iodide and a highly active and alkaline solution of a tracer containing sodium iodide. The labeled ^{131}I CH_3I aqueous solution at a desired concentration was then prepared by dissolving the tagged CH_3I in boric-acid/borate solution to achieve the required pH (5–9) in the reaction vessel. A certain amount of concentrated aqueous solution of the additive(s) was then introduced for the designated experiment. The solution volumes for all experiments were constant.

Determination of iodine species generated after the irradiation

Iodine speciation after a pre-defined irradiation period, i.e., volatile iodine species having remained or generated during irradiation, was determined either (1) by removing them by gas sparging, and then absorbing in special selective solid-phase absorbers or (2) by examination² of the reaction vessel solution for the presence of iodide and iodate and for molecular iodine and methyl iodide. The specific measurements determining the iodine speciation provided the extent of decomposition and as well as attendant reactions.

Results and discussion

CH_3I decomposition by hydrolysis

Experiments were conducted under the following conditions: air-saturated solutions; pH range: 5–9; CH_3I concentration range: 10^{-6} – 10^{-3} mol·dm⁻³; temperature range: 22–90 °C.

Results show that, in the temperature range 20 to 70 °C, CH_3I hydrolysis alone is too slow for efficient decomposition. For example, after 6 days at 22 °C, only about 4% of the CH_3I had decomposed, after 1.5 hours at 50 °C, this was only 0.4%; and, after 45 minutes at

70 °C, just 13%. At high temperatures (>100 °C) the rate is increased by a factor of about 10^4 .

The deduced rate constants were compared (Fig. 2) against data from the literature.³ As can be seen, the correlation between measured and literature data is satisfactory. The negligible CH_3I hydrolysis, observed at room temperature, allows for easy investigation of decomposition due to other effects (i.e., additives and radiation).

CH_3I decomposition by radiolysis

Radiation absorbed in water produces a number of primary species: e^-_{aq} , $\cdot\text{H}$, $\cdot\text{OH}$, H_2O_2 , H_2 and H^+ . The solvated electrons (e^-_{aq}) or hydrogen atoms ($\cdot\text{H}$) reduce CH_3I to form methyl radicals ($\cdot\text{CH}_3$), I^- and H^+ . Reference 4 indicates that the oxidizing hydroxyl radicals ($\cdot\text{OH}$) and the reducing superoxide ($\cdot\text{O}_2^-$) do not react with CH_3I . PSI results show a proportional decomposition of CH_3I with dose, and suggest also that complete decomposition is achieved after a dose of 3.1 kGy at 22 °C. A proportional dependence between the yield of radiolytic decomposition [$G(-\text{CH}_3\text{I})$] and the initial CH_3I concentration has already been quantitatively established:⁵ $G(-\text{CH}_3\text{I}) = 561.8 \times C$ where G is in $\mu\text{mol}\cdot\text{J}^{-1}$, and C is the concentration of CH_3I in mol·dm⁻³. Our data correlates with this dependence (Fig. 3). Data from experiments performed at 50 °C were, within the detection limits, identical to those at room temperature. The weak dependence of radiolysis on temperature may, therefore, be used as an offset to determine the effect of temperature on the effectiveness of the additives on the decomposition process (see below). The results indicate that the decomposition by radiolysis compared with hydrolysis is only important at low temperatures (<70 °C), or at high dose rates (>0.1 kGy/h).

CH_3I decomposition by additives

Literature and our experimental data do not support an effective and fast decomposition rate by the resident processes in the containment sump under the relevant accident boundary conditions. In order to achieve either a much higher transfer rate from the containment atmosphere containing organic iodides into the water or the smallest release rate from the water into the atmosphere, the concentration gradient between the phases should be maximized for all postulated conditions. This can be achieved only by rapid decomposition of the volatile species in the water phase. Other chemical agents (additives) are, therefore, needed to increase the overall decomposition rate. Additives with sufficient thermal, radiolytical stability and usability in the pH range 3 to 9 were selected.

They must also not suppress the thermal and radiolytic decomposition of CH_3I . A non-volatile iodine species (preferably iodide) as the main decomposition product over a range of relevant pH and CH_3I concentrations was also an objective. Furthermore, molecular iodine, if formed or transferred into water, should be reduced to iodide ions very efficiently. The main issue to resolve was to find additives, which not only cause rapid decomposition but enable effective fixation of non-volatile species by precipitation or absorption to prevent rapid conversion to I_2 under oxidizing conditions.

Additives selected were:

(1) Additives, which react by (thermal) bi-molecular nucleophilic substitution ($\text{S}_{\text{N}}2$): e.g., $\text{Na}_2\text{S}_2\text{O}_3$, $(\text{NH}_4)_2\text{S}$, $\text{N}_2\text{H}_5\text{OH}$.

(2) Additives, which produce other reductants from $\bullet\text{OH}$ radicals, will enhance CH_3I decomposition since CH_3I is not decomposed in irradiated water by generated $\bullet\text{OH}$ radicals, but only by the strong reductants e^-_{aq} and $\bullet\text{H}$, e.g., sodium formate.

A second additive consisting of a liquid quaternary ammonium compound, trioctylmethylammonium chloride (Aliquat 336) was also tested. It has a dual function by acting as:

(1) a phase-transfer catalyst,⁶ i.e., to enhance the rate of a nucleophile–methyl iodine reaction and

(2) an anionic-exchanger exchanging an iodide ion for a chloride ion.

The irradiation and non-irradiation experiments were conducted for a fixed contact time (45 minutes) of the additives with CH_3I .

The results of the irradiation experiments containing additives confirm that radiolytic and nucleophilic decomposition of CH_3I are two independent and complementary processes. However, the results suggest that further use of Aliquat 336 as a co-additive could act in the second step of a two-step process: i.e., CH_3I is first radiolytically decomposed into iodide ions, which are then exchanged for chloride ions by Aliquat 336. The latter concentrates the reactants, i.e., the thiosulphate ions and CH_3I molecules, and hence, enhances decomposition (Fig. 4). This combined process appears to prevent, or very largely suppresses, the radiolytic oxidation of the iodide ions to I_2 . The experimental results show an almost complete CH_3I decomposition at high pH, different temperatures and initial CH_3I concentrations, using both an additive (sodium thiosulphate) and a co-additive (Aliquat 336) at the studied additive concentrations. The results have also demonstrated the very efficient suppression of I_2 formation.

Fig. 1. Experimental facility and analytical techniques

Fig. 2. Comparison of CH_3I hydrolysis rate constants measured and from literature³

Fig. 3. Radiation yield $[G(-\text{CH}_3\text{I})]$ dependence on initial CH_3I concentration

Fig. 4. Effect of additives on the destruction of methyl iodide

Conclusions

The PSI results have provided new data on iodine behavior under conditions not previously studied, but which are of direct relevance to severe accidents in both Pressurised Water Reactor (PWR) and Boiling Water Reactor (BWR) systems.

The use of an additive pair has shown that a very significant enhancement of decomposition of organic iodide can be achieved. Further experiments are necessary to investigate potential interference from sump constituents on the observed decomposition rates as well as to study the effect of large irradiation doses on the stability of these additives.

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