Article:

Pepper, S.E. orcid.org/0000-0002-8570-3156, Baker, A., Maher, C.J. et al. (3 more authors) (2024) Iodine behaviour in spent nuclear fuel dissolution. Progress in Nuclear Energy, 169. 105062. ISSN: 0149-1970

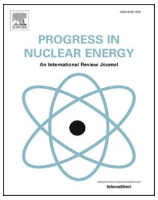
https://doi.org/10.1016/j.pnucene.2024.105062

Progress in Nuclear Energy 169 (2024) 105062

Contents lists available at ScienceDirect

Progress in Nuclear Energy

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



Iodine behaviour in spent nuclear fuel dissolution

Sarah E. Pepper[a,*,1], Alastair Baker[a], Chris J. Maher[b], Mike J. Carrott[b], Joshua Turner[b], Bruce C. Hanson[a]

[a] School of Chemical and Process Engineering, University of Leeds, Leeds, United Kingdom
[b] National Nuclear Laboratory, Central Laboratory, Sellafield, Seascale, Cumbria, United Kingdom

ARTICLE INFO

Keywords:
Iodine
Fission products
Dissolution
Spent nuclear fuel
Reprocessing

ABSTRACT

The chemistry of iodine in spent nuclear fuel (SNF) solutions is extremely complex and numerous species have been identified. These include iodine (I_2), iodide (I^-), iodate (IO_3^-), triiodide (I_3^-) and insoluble colloidal compounds with the fission products silver and palladium (AgI and PdI_2). The experimental parameters that control the removal of iodine from SNF solutions are poorly understood. Experiments were performed at two temperatures representative of dissolver conditions. It was found that iodine, added as iodide, was rapidly removed from solution; within 30 s over 70% and 90% of the initially added amount was removed at 60 and 80 °C, respectively.

1. Introduction

A nuclear renaissance is predicted in response to the need to significantly reduce greenhouse gas emissions and decarbonise the economy, with a target of net zero adopted by many countries to combat global climate change (LifeCycle Assessment of Electricity Generation; The Paris Agreement). In the UK, it has been predicted that the net zero target set for 2050 cannot be met unless nuclear power production is significantly increased, supported through investment in new build, such as at Hinckley Point C, and investment in developing and maintaining fuel cycle capabilities (Energy White Paper). To minimise the environmental and human health impacts of the nuclear industry, it is expected that releases of iodine, as well as other species, will be more tightly controlled. Specifically for iodine, the chemical processes occurring are not completely understood, in part due to the complexity of its chemistry. We have presented a brief overview of iodine chemistry in different systems, including the nuclear fuel cycle, to highlight its complex chemistry, before presenting the results of a series of experiments performed in simplified simulated nuclear fuel dissolver solutions in an effort to better understand the chemical controls on iodine removal from aqueous solutions.

1.1. Iodine in the environment

Iodine, atomic number 53, is an important trace element, found in the hydrosphere, lithosphere, atmosphere and biosphere; with the oceans representing the largest source (>70%), where it is present as dissolved iodide (I^-). It is also an essential trace element for humans and all vertebrates, used to make thyroid hormones, which control the body's metabolism and other important functions. Thyroid hormones are also needed for proper bone and brain development during pregnancy and infancy (Chung, 2014; Fuge and Johnson, 2015).

Its chemistry is extremely complicated both in solution and in the gas phase, in part because it can exist in multiple oxidation states, ranging from −1 to +7. Some of the inorganic species found in solution are shown in Table 1.

The geochemistry of iodine is dominated by its volatility (Fig. 1), with the volatilisation of inorganic iodine species and organo-iodide compounds in the oceans representing a major component of its global cycle, releasing about 400,000 tonnes annually (Fuge and Johnson, 2015; Koenig et al., 2020; Whitehead, 1984; Hou et al., 2009; Amachi, 2008). Once in the atmosphere, these species can undergo a series of reactions resulting in gaseous and particulate forms (Saiz-Lopez et al., 2014; Chameides and Davis, 1980; Wayne et al., 1995; Read et al., 2008; Sherwen et al., 2016a).

While these species can be deposited on land and become part of the biosphere (Whitehead, 1984), they also play an important role in atmospheric chemistry, where they can lengthen the lifetime of methane, a potent greenhouse gas (Sherwen et al., 2016b) and form new particles, which in turn lead to the formation of cloud condensation nuclei

---

* Corresponding author.
E-mail address: sarah.pepper@sheffield.ac.uk (S.E. Pepper).

[1] Current address: Department of Materials Science and Engineering, University of Sheffield, Sheffield, United Kingdom.

https://doi.org/10.1016/j.pnucene.2024.105062
Received 30 May 2023; Received in revised form 20 November 2023; Accepted 9 January 2024

Table 1
Commonly found species of inorganic iodine in the aqueous phase, their oxidation states and names. Please note this list is not exhaustive, as iodine can form other species, such as I_2O and various organo-iodine species, depending on pH and concentration.

Formula	Oxidation state	Name
I^-	−1	Iodide
I_3^-	−1	Triiodide
I_2	0	Iodine
HOI	+1	Hypoiodous acid
IO^-	+1	Hypoiodite
H_2OI^+	+1	Hypoiodous acidium
HIO_2/$HOIO$	+3	Iodous acid
IO_2^-	+3	Iodite
HIO_3	+5	Iodic acid
IO_3^-	+5	Iodate
HIO_4	+7	Periodic acid
IO_4^-	+7	Periodate

(O'Dowd et al., 2002). Iodine has also been reported to contribute to climate change through the catalytic destruction of ozone (O_3) in the atmosphere as iodine reacts with ozone to produce iodine monoxide (IO), similar to other halogens like bromine and chlorine. An example of the reactions which can participate in the destruction of ozone are shown below, where X = Cl, Br or I (Chameides and Davis, 1980; Sherwen et al., 2016b):

$$O_3 + X \rightarrow XO + O_2 \tag{1}$$

$$HO_2 + XO \rightarrow HOX + O_2 \tag{2}$$

$$HOX + h\nu \rightarrow OH + X \tag{3}$$

However, the rate of iodine ozone destruction has been reported to be a million times faster than for other halides, greater than 600 times that of chlorine (Koenig et al., 2020). Whilst this process occurs naturally, iodine levels measured in ice-core samples from East Greenland have tripled from 1950 to 2011, likely as a result of anthropogenic ozone pollution. These increased atmospheric iodine levels in turn lead to tropospheric and stratospheric ozone loss (Koenig et al., 2020; Sherwen et al., 2016b; Cuevas et al., 2018; Prados-Roman et al., 2015).

1.2. Iodine in aqueous solutions

The chemistry of iodine in aqueous solution is complicated and the species present depend on the concentration and pH of the solution, as shown in the speciation diagram in Fig. 2. The main reactions that occur in solution are discussed below. In aqueous solution, iodine undergoes hydrolysis and disproportionation, according to the following Reaction (4), producing iodate (IO_3^-) (Tsukaue et al., 1994; Paquette and Ford, 1985; Nagy et al., 2003; Thomas et al., 1980; Sebők-Nagy and Körtvélyesi, 2004; Palmer et al., 1984a):

$$3I_2 + 3H_2O \leftrightarrow 5I^- + IO_3^- + 6H^+ \tag{4}$$

However, this reaction is in fact a two-step reaction involving the generation of hypoiodous acid (HOI) as an intermediate:

$$I_2 + H_2O \leftrightarrow HOI + I^- + H^+ \tag{5}$$

The hypoiodous acid decomposes producing iodate and iodide:

$$3HOI \rightarrow 2I^- + IO_3^- + 3H^+ \tag{6}$$

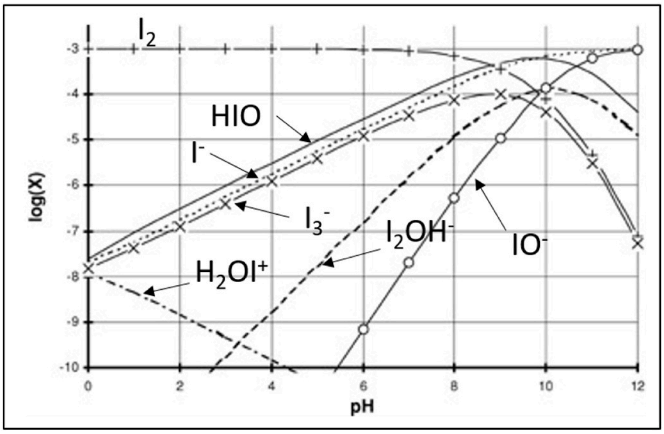


Fig. 2. Speciation diagram of iodine at a total concentration of 1 × 10^{-3} M. Adapted from (Schmitz, 2004).

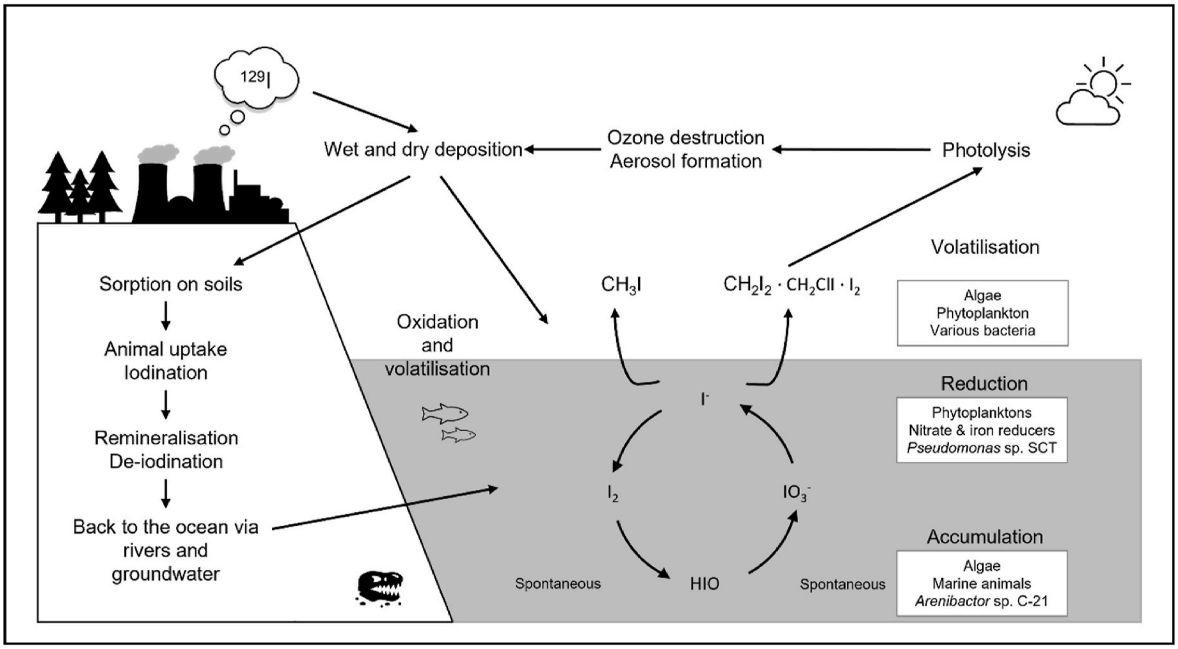


Fig. 1. The environmental cycling of iodine (Amachi, 2008).

Table 2

Various reactions for iodine hydrolysis and related reactions in aqueous solutions with their equilibrium constants. Values present in 1 are taken from (Schmitz, 2004), while those in 2 are from other sources. Reaction numbers relate to the reactions presented in the text.

Reaction	Eqm. Const. at 25 °C			Rxn. No.
	1	2		
$I_2 + H_2O \leftrightarrow HOI + I^- + H^+$	$K_1 = 5.3 \times 10^{-13}$ M^2	$K_1 = 5.44 \times 10^{-13}$ M^2	Truesdale et al. (2003)	5
$I_2 + H_2O \leftrightarrow I_2OH^- + H^+$	$K_2 = K_1/K_4 = 1.7 \times 10^{-10}$ M	$K_2 = 1.41 \times 10^{-11}$ M	Truesdale et al. (2003)	
$I_2 + OH^- \leftrightarrow I_2OH^-$	$K_3 = K_2/K_w = 1.7 \times 10^4$ M^{-1}			
$I_2OH^- \leftrightarrow HOI + I^-$	$K_4 = 3.1 \times 10^{-3}$ M			
$I_2 + I^- \leftrightarrow I_3^-$	$K_5 = 715$ M^{-1}	$K_5 = 729$ M	Truesdale et al. (2003)	7
$H_2OI^- \leftrightarrow HOI + H^+$	$K_6 = 2$ M			
$HOI \leftrightarrow IO^- + H^+$	$K_7 = 2.3 \times 10^{-11}$ M	$K_7 = 2.5 \times 10^{-11}$ M	Truesdale et al. (2003)	9
$I_2 + H_2O \leftrightarrow H_2OI^+ + I^-$	$K_8 = K_1/K_6 = 2.6 \times 10^{-13}$ M	$K_8 = 1.25 \times 10^{-11}$	Paquette and Ford (1985)	8
$H_2O \leftrightarrow H^+ + OH^-$	$K_w = 10^{-14}$ M			

The first step, Reaction (5), has been reported to be rapid and diffusion controlled while the second step Reaction (6) is believed to be slower. It can take hours or days depending on the pH, temperature, concentration and presence of other solute molecules (Thomas et al., 1980) and has been reported to be a second-order reaction (Wren et al., 1986). The equilibrium constant, K_1, for Reaction (4) has been calculated at 25 °C and an ionic strength of 0.2 M ($NaClO_4$) in buffered solution as $\log K_1 = -47.61 \pm 0.07$ (Nagy et al., 2003) and -46.93 using a potentiometric methodology (Palmer et al., 1984b).

In alkaline media, Reaction (4) is rapid, but slows down with increasing acidity (Nagy et al., 2003). While at high acidities, the reverse of Reaction (4), named the Dushman reaction, is reported to be relatively fast. This is due to the presence of protons [H^+]. At low acidity, the reaction becomes slower, as the equilibrium is not shifted completely to the left.

The chemistry of iodine is further complicated by an additional reaction between I_2 and I^-, shown in Reaction (7) (Tsukaue et al., 1994; Thomas et al., 1980; Palmer et al., 1984b):

$$I_2 + I^- \leftrightarrow I_3^- \tag{7}$$

Similar to Reaction (5), this reaction is believed to be diffusion controlled (Thomas et al., 1980). The equilibrium constant for this reaction at 25 °C has been determined as 698 ± 10 (Palmer et al., 1984a). Furthermore, I_2 can react in solution as follows (Paquette and Ford, 1985):

$$I_2 + H_2O \leftrightarrow H_2OI^+ + I^- \tag{8}$$

The equilibrium constant (K_8) for this reaction was calculated as 1.25×10^{-11} at 25 °C with a pKa value of 1.4 ± 0.3 for H_2OI^+ and was later revised to $K_8 = 2.6 \times 10^{-13}$ (Schmitz, 2004). Below pH 2, the protonation of HOI is significant and iodine hydrolysis becomes independent of pH at pH < 0, with the stoichiometry of iodine hydrolysis then given by Reaction (10), shown below (Lengyel et al., 1993).

Between pH values of 7 and 10, disproportionation of iodine is reported to occur via HOI as the reactive intermediate (Thomas et al., 1980), with HOI itself forming via an intermediate, I_2OH^- (Eigen and Kustin, 1962). The pKa of HOI is 10.0 ± 0.3 (Paquette and Ford, 1985). Additionally, HOI can dissociate in alkaline media according to either of the following two reactions (Paquette and Ford, 1985; Thomas et al., 1980; Urbanski et al., 1997):

$$HOI \leftrightarrow H^+ + IO^- \tag{9}$$

$$5HOI \leftrightarrow 2I_2 + IO_3^- + H^+ + 2H_2O \tag{10}$$

Reaction (10) is rapid, as within 5 s, the time taken to mix the components, I_2 was reported to already be present (Paquette and Ford, 1985). It has been reported that there is widespread agreement in the literature that this reaction is second-order with respect to hypoiodous concentration, although a large range of rate constants has been reported, from 5.6 to 250 $M^{-1}s^{-1}$ (Urbanski et al., 1997). One reason given for the variation was that the reaction exhibits very complex behaviour. Table 2 summarises the main reactions that can occur in solution and their equilibrium constants.

1.3. Radiochemistry of iodine

Iodine has only one stable isotope, ^{127}I, and forty-six radioactive isotopes. The majority are produced as a result of nuclear fission, while some are generated for nuclear medicine. It should be noted that while ^{129}I is generated as a result of nuclear fission, it occurs naturally as does ^{127}I. Most radioactive isotopes of iodine have relatively short-half-lives, from ns to hours (Lin et al., 2009; National Nuclear Data Center) but ^{129}I and ^{131}I are of particular concern, due to their half-lives of 15.7 million years and 8 days, respectively. ^{129}I presents an obvious long-term hazard and is associated with the disposal and storage of SNF (Hou et al., 2009;

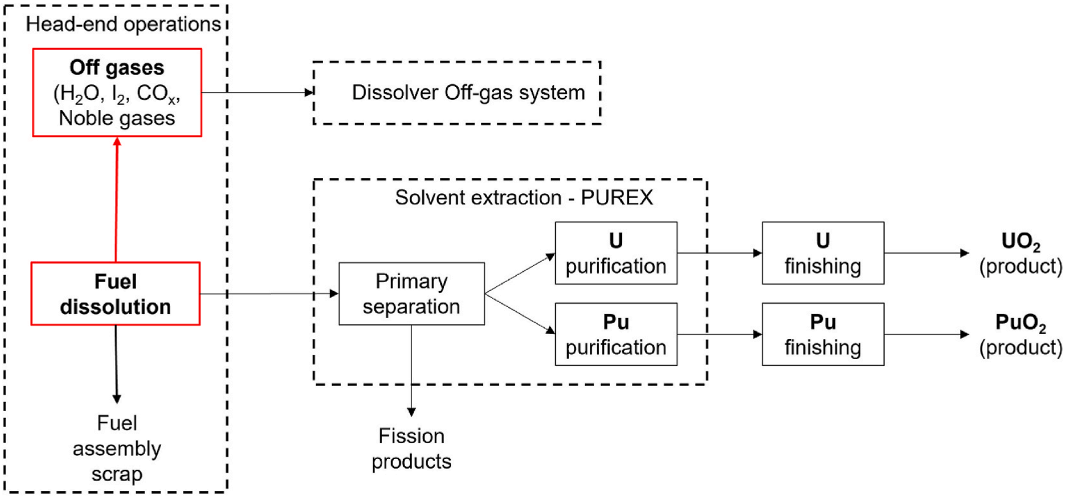


Fig. 3. Simplified schematic representation of the reprocessing of SNF.

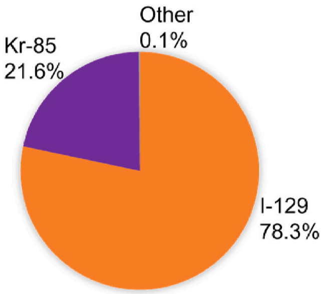


Fig. 4. Radionuclide biological impact from aerial discharges from THORP (Paulilo et al., 2020).

Guido-Garcia et al., 2015), while ^{131}I presents a short-term hazard to exposed individuals as a result of its high specific activity and prevalence for concentrating in the thyroid (over 90% of the body's iodine is found in the thyroid) (Amachi, 2008; Kara et al., 2014). As ^{131}I decays, the surrounding tissue is subjected to beta particles, which promote thyroid cancer. Its release is more often associated with accidents or failures at nuclear facilities, for example the Chernobyl accident in 1986 and the Fukushima Daiichi accident in 2011. After the Chernobyl accident, the majority of the radiation emitted in the first week was found to be ^{131}I. After the Fukushima Daiichi accident, ^{131}I was found in rainwater and milk samples in the western USA (Hu et al., 2012).

1.4. Iodine in spent nuclear fuel solutions

^{129}I, in addition to being emitted during nuclear accidents and failures, is produced in appreciable amounts during nuclear fission, the bombardment of uranium and/or plutonium nuclei with neutrons resulting in the splitting of the element and the release of energy. It and other iodine isotopes combine with more electro-positive fission product elements, especially caesium, of which there is a large amount, forming caesium iodide. One tonne of SNF from a pressurised water reactor accumulates 200–300 g of I at an average fuel burn-up rate of 45 GW day t^{-1} (Kulyuknin, 2012). Once SNF is removed from the reactor, it is typically stored for up to 5 years and during this time the shorter-lived radionuclides of iodine have decayed, including ^{131}I, leaving ^{129}I. In an open nuclear cycle, the fuel passes through a reactor once and the SNF is classified as waste and sent to disposal. In a closed nuclear cycle, the SNF, which contains a significant amount of unused fissile material, is reprocessed and recycled. Reprocessing involves several steps, including head-end operations, separation (PUREX) and finishing and disposal (Fig. 3). During head-end operations, SNF is removed from its casing and chopped into smaller pieces (shearing prior to dissolution in 3.0–8.0 M nitric acid) (Berry et al., 1987; Sakurai et al., 1996). Whilst some of the iodine remains with the fuel matrix, some is redistributed and forms caesium iodide, which is non-volatile under standard reprocessing temperatures and therefore iodine is not released during the shearing process (Konings et al., 2015; Heikinheimo et al., 2021; Saidy et al., 2008). It is released during dissolution by oxidation of iodide by nitric (HNO_3) and nitrous acids (HNO, HNO_2), Reactions (11) and (12), followed by volatilisation to gaseous iodine, Reaction (13) (Leudet et al., 1983; Sakurai et al., 1997).

$$I^- + 2H^+ + NO_3^- \leftrightarrow 0.5I_{2(aq)} + NO_2 + H_2O_{(l)} \tag{11}$$

$$I^- + 4H^+ + NO_2^- + 2NO_3^- \leftrightarrow 0.5I_2 + 3NO_2 + 2H_2O_{(l)} \tag{12}$$

$$I_{2(aq)} \leftrightarrow I_{2(g)} \tag{13}$$

Over 90% of the iodine present in SNF is volatilised to the dissolver off-gas system at this point, with the actual amount depending on (Berry et al., 1987; Leudet et al., 1983; Riley et al., 2016; Sakurai et al., 1989):

a) Carrier gas flow
b) Presence of NO_2
c) Solute concentration
d) Formation of non-volatile compounds

As much iodine as possible is removed during head-end operations to simplify iodine control and to minimise the amount continuing downstream, where it can interfere with the different processes and/or be released. For example, it has been found in tributyl phosphate/odourless kerosene (TBP/OK) solutions, the solvent used during the PUREX process, as a contaminant, either as an organo-iodide species or as iodine (Reed et al., 2002). It can then be volatilised during waste solvent pyrolysis. In the United Kingdom, at the THORP facility (Thermal Oxide Reprocessing Plant), which operated from 1994 to 2018, undissolved residues were encapsulated, including a small proportion of iodine present as noble metal iodides. Future reprocessing schemes could aim to reduce the number of waste forms, however if these solids were diverted to HLW plants, the undissolved solids containing iodine would be thermally decomposed and released in the highly active waste melter off-gas during vitrification (Jubin et al., 2013). The iodine released during head-end operations could be captured and treated in the dissolver off-gas (DOG) system using a silver-based solid adsorbent (Jubin et al., 2013; Umadevi and Mandal, 2021; Wiechert et al., 2020; Abney et al., 2017). The resulting silver adsorbent must be conditioned into a waste form with suitable long-term durability (Riley et al., 2016). For this reason, historically, iodine has been treated and discharged to sea, and to a lesser extent aerially (IAEA, 2014). For example, at the THORP facility, ^{129}I emissions in terms of radioactivity were lower than other radionuclides, such as ^{85}Kr (Hudson et al., 1996) but the higher biological accumulation rates of iodine results in ^{129}I dominating the aerial discharge impact (Fig. 4). Improved control of ^{129}I could aim to reduce the radiotoxicity of discharges in the future. THORP also released iodine to the environment as aqueous discharges to the Irish Sea (Paulilo et al., 2020).

For the iodine remaining in solution, its composition depends on several factors, with the presence of fission products (FPs) appearing to have a major influence on the speciation. In the absence of FPs, the composition of the residual solution comprises 90% iodate and 10% iodine (Sakurai et al., 1989, 1993, 1996). Iodine, produced during the dissolution of SNF (Reactions 11 and 12), is converted to iodate according to:

$$I_{2(aq)} + 8H^+ + 10NO_3^- \rightarrow 2IO_3^- + 10NO_{2(g)} + 4H_2O \tag{14}$$

The addition of iodide to a simulated spent nuclear fuel solution in 3.4 M nitric acid at 100 °C resulted in 93.3–98.5% being volatilised to iodine, with iodate reported to be the dominant species remaining in solution (Sakurai et al., 1989). The iodide was converted according to the following reactions:

$$2H^+ + 2I^- + HNO_3 \rightarrow HNO_2 + I_2 + H_2O \tag{15}$$

$$2I^- + 5HNO_3 + H_2O \rightarrow 7H^+ + 2IO_3^- + 5NO_2 \tag{16}$$

Nitrogen dioxide can reduce iodate to iodine (Riley et al., 2016). It is present in nitric acid solutions and is also passed through the dissolver solution to alter the oxidation state of plutonium to + IV to facilitate a more efficient extraction with uranium during the PUREX process. Its formation in 3.5 M nitric acid solution at 100 °C occurs via (Sakurai et al., 1993):

$$2H^+ + 2NO_3^- \rightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)} + H_2O_{(l)} \tag{17}$$

It should be noted that this study commented that the amount of NO_2 in dissolver solutions at 100 °C may be higher than has been reported by other workers as the amount increases with increasing temperature, from P_{NO2} at 4% at 25 °C to 80 % at 100 °C. The amount of NO_2 is usually extrapolated from the amounts calculated from the dissolver off gas,

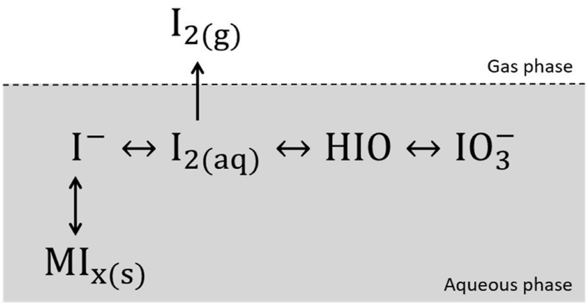


Fig. 5. Iodine species commonly expected in SNF dissolver solutions. Adapted from (Maher and Taylor, 2015).

which is measured at room temperature (Sakurai et al., 1993). Sparging a simulated SNF solution with NO_2 (~10 % in N_2 at a flow rate of 30 mL/min), reduced iodate to iodine resulting in >99 % of the added iodide being easily expelled from the solution (Sakurai et al., 1989):

$$2H^+ + 2IO_3^- + 10NO_2 + 4H_2O \rightarrow 10HNO_3 + I_2 \tag{18}$$

in addition to iodate and iodine in dissolver solutions, iodide, tri-iodide, iodic acid and organo-iodides (for example CH_3I and C_2H_5I) have also been identified (Tsukaue et al., 1994; Riley et al., 2016; Soelberg et al., 2013; Kireev and Shnyrev, 2015). Organo-iodides can form due to impurities in the nitric acid present from the manufacturing process, however THORP dissolvers didn't use nitric acid recovered from solvent extraction process operations. However, recycling and recombination of nitric acid could increase the organic content of nitric acid (Jubin et al., 2013). Sparging a solution with 1–2 vol% NOx gas resulted in the tri-iodide and iodide ions forming iodine, via oxidation from HNO_2 or HNO_3. These are formed in solution from the reaction between NO_2, contained in NOx, and water (Tsukaue et al., 1994):

$$2NO_{2(g)} + H_2O_{(l)} \rightarrow NO_2^- + NO_3^- + 2H^+ \tag{19}$$

A recent study investigating the dissolution of SNF in 2–4 M nitric acid suggested that molecular iodine is formed from metallic iodine in the fuel. Metallic iodine reacts with water, rather than nitric acid (Kireev and Shnyrev, 2015):

$$2I + H_2O \rightarrow I_2 + H_2O \tag{20}$$

Reactions (5), (6) and (9) were reported to also occur, along with the following:

$$3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO\uparrow + 2H_2O \tag{21}$$

$$HIO_3 \rightarrow H^+ + IO_3^- \tag{22}$$

The dissociation of iodic acid (HIO_3), Reaction (22), is rapid and results in the formation of iodate ions, which are, therefore, the first to be formed in solution. Reactions (5) and (7) are rapid, while Reaction (6) is much slower causing iodide and tri-iodide to be formed last (Kireev and Shnyrev, 2015).

One study looking at medical isotope production reactors found that iodide, in a $UO_2(NO_3)_2$–HNO_3 solution (50 g/L UO_2^{2+} and 0.2 M HNO_3) was oxidised to iodine and iodate (Qi-min et al., 2009). The amount of iodine and iodate produced increased with increasing heating time and temperature. The maximum amount of iodide and iodate, 10.5% and 83% respectively, was produced after heating for 6 h at 70 °C. Increasing the concentration of nitric acid increased the amount of iodate formed and decreased the amount of iodine consistent with the following process:

$$I^- \rightarrow I_2 \rightarrow IO_3^- \tag{23}$$

They also reported that oxidants other than nitric acid, such as H_2O_2, could also accelerate the oxidation of iodide to iodine and iodine to iodate (Qi-min et al., 2009).

Another study looking at iodine (1×10^{-4} M) in a uranyl nitrate-nitric acid solution (0.21 M $UO_2(NO_3)_2$–3.4 M HNO_3) found that iodine was oxidised to iodate under room lights (Paulilo et al., 2020). In the absence of uranyl nitrate, only 20% of iodine was oxidised, whereas in its' presence, 95 % of the iodine was oxidised. Solutions of iodine-nitric acid (0.9×10^{-4} M $I_{2(aq)}$ – 3.5 M HNO_3) in the absence and in the presence of uranyl nitrate (0.21 M) kept in the dark for 18 h prior to exposure to an argon ion laser at 457.9 nm exhibited similar behaviour. Decreasing the concentration of uranyl did not cause a significant

Table 3
Concentration of different species expected in the dissolver and the values used in these experiments.

Species	Values in dissolver (M)	Experimental values (M)
Iodine (as iodide)	1.2×10^{-3}	2.1×10^{-4}
Nitric acid	4.0	4.0
Silver (Ag^+)	5.19×10^{-4}	9.25×10^{-5}
Palladium (Pd^{2+})	0.012	2.15×10^{-3}

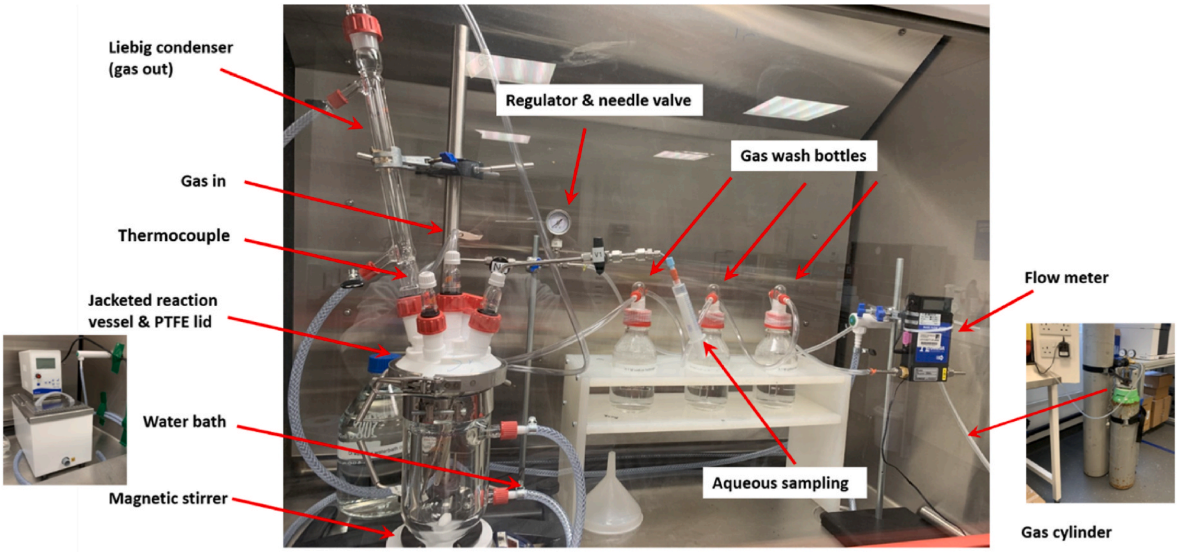


Fig. 6. Iodine removal experimental reaction rig, simulating a SNF dissolver.

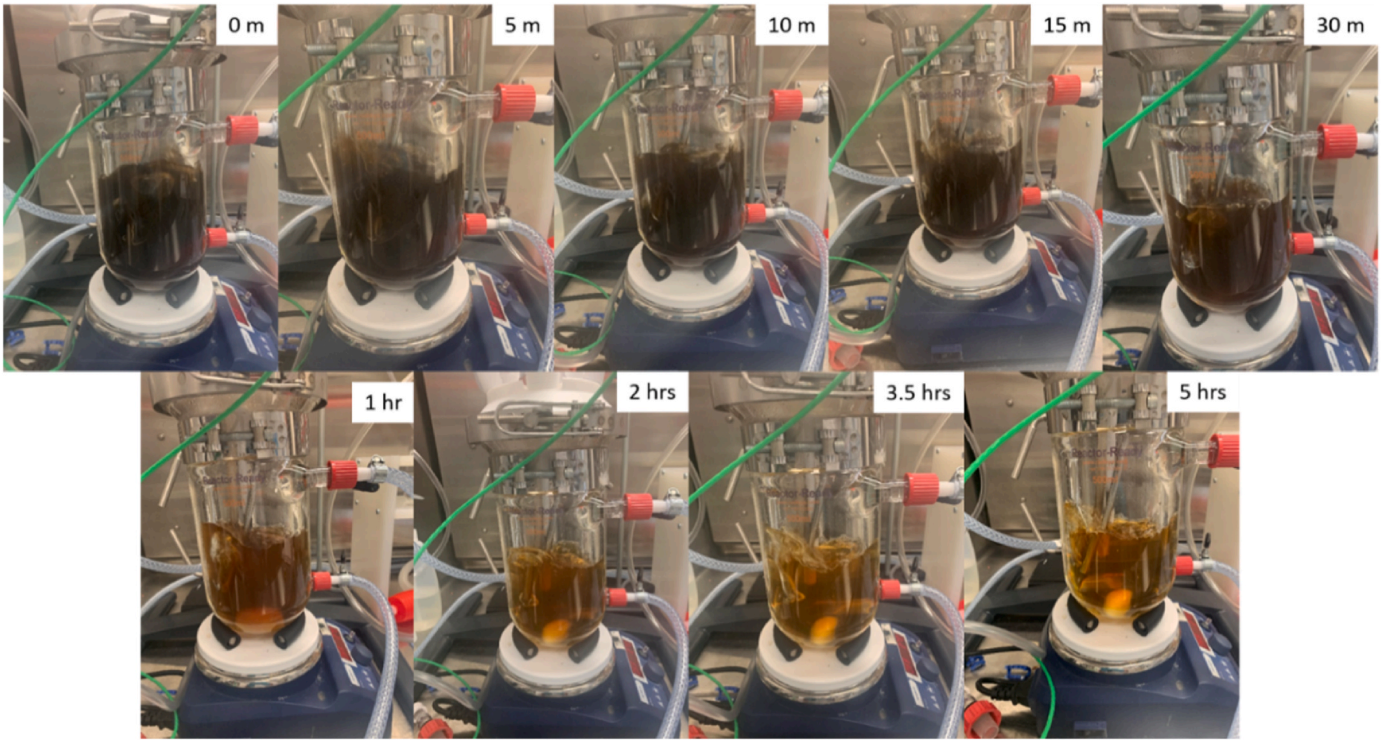


Fig. 7. Iodide (2.1×10^{-4} M) in the presence of fission products silver (9.25×10^{-5} M) and palladium (2.15×10^{-3} M) in 4.0 M HNO_3 at 60 °C.

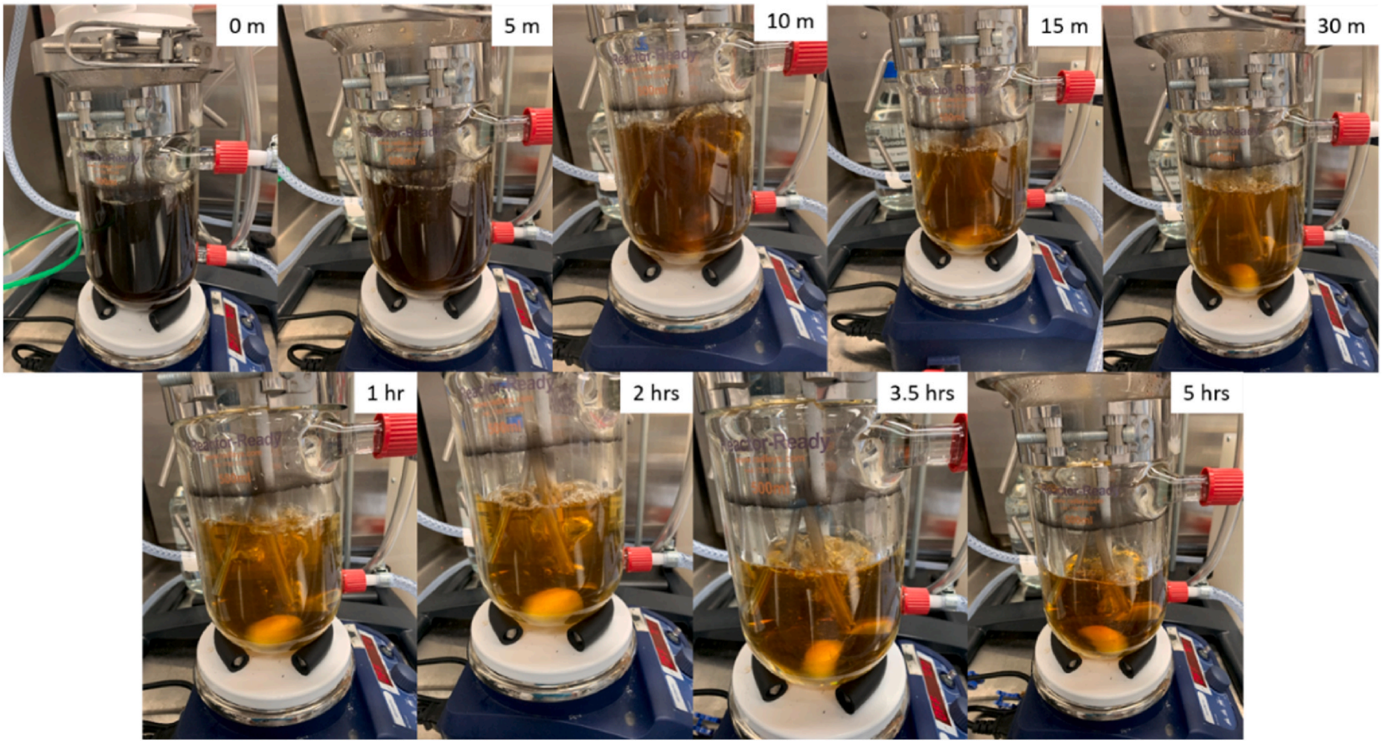


Fig. 8. Iodide (2.1×10^{-4} M) in the presence of fission products silver (9.25×10^{-5} M) and palladium (2.15×10^{-3} M) in 4.0 M HNO_3 at 80 °C.

decrease in the rate of iodine oxidation, while decreasing the nitric acid concentration from 3.5 M to 0.5 M almost stopped the reaction. The study concluded that while oxidation of iodine was due to nitric acid, photo-excited uranyl accelerated the reaction (Sakurai, 1996). This suggests that in highly active solutions, where radiolysis occurs, this phenomenon needs to be examined.

The result of nuclear fission is that SNF contains almost all the elements of the Periodic Table below uranium, termed fission products (FPs) and their presence complicates the solution chemistry. For iodine, palladium and silver have been identified as the FPs that cause the most problems, through the formation of non-volatile colloidal iodides, PdI_2 and AgI (Sakurai et al., 1989). Other FPs like lanthanum, strontium,

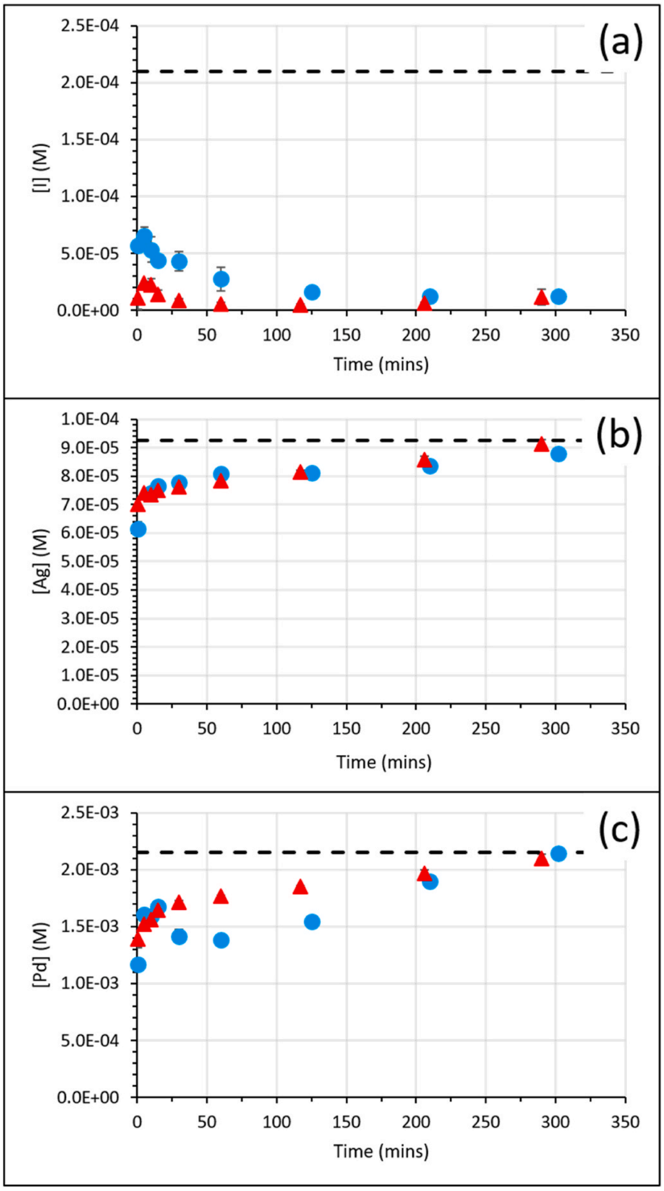


Fig. 9. ICP-MS results for (a) iodine, (b) silver and (c) palladium remaining in solution in 4.0 M HNO_3 at 60 and 80 °C (blue circles and red triangles, respectively). The dashed line represents the initial concentrations. Error bars represent the error associated with triplicate measurements from ICP-MS analysis.

barium and cerium do not appear to generate colloidal iodides. In experiments with simulated SNF, it was found that 60% of the iodine was present as colloidal iodides, 20% as iodine and 20% as iodate (Sakurai et al., 1993, 1997). The colloidal species are formed according to (Sakurai et al., 1996):

$$Pd^{2+} + 2I^- \rightarrow PdI_{2(s)} \tag{24}$$

$$Ag^+ + I^- \leftrightarrow AgI_{(s)} \tag{25}$$

They partially dissolve in hot nitric acid:

$$PdI_2 + 4HNO_3 \rightarrow I_2 + Pd(NO_3)_2 + 2NO_2 + 2H_2O \tag{26}$$

$$2AgI + 4HNO_3 \rightarrow I_2 + 2AgNO_3 + 2NO_2 + 2H_2O \tag{27}$$

It was reported that if the colloids age, their dissolution rates or reactions with HNO_3 are reduced, hindering their removal, although no explanation was given as to why colloid ageing impacts their removal.

NO and NO_2 have been reported to suppress the formation of these colloidal iodides in proportion to their concentration up to about 10% (Sakurai, 1996). Above this concentration, NO_2 interferes with the decomposition of the already formed colloid by reversing Reactions (26) and (27) (Sakurai et al., 1995, 1997), suggesting these reactions should be presented as:

$$PdI_2 + 4HNO_3 \leftrightarrow I_2 + Pd(NO_3)_2 + 2NO_2 + 2H_2O \tag{28}$$

$$2AgI + 4HNO_3 \leftrightarrow I_2 + 2AgNO_3 + 2NO_2 + 2H_2O \tag{29}$$

The addition of iodate to the NO_2 sparge can cause iodate to decompose PdI_2 and AgI to iodine, according to (Sakurai et al., 1989):

$$5PdI_2 + 2HIO_3 + 10HNO_3 \rightarrow 6I_2 + 5Pd(NO_3)_2 + 6H_2O \tag{30}$$

$$5AgI + HIO_3 + 5HNO_3 \rightarrow 3I_2 + 5AgNO_3 + 3H_2O \tag{31}$$

This study concluded that a high iodate concentration in the solution was important to minimise the amount of colloidal iodides. This could be achieved by increasing the nitric acid concentration from 3.4 M to 6.1 M (Sakurai et al., 1989). It has been reported that nitrous acid, up to a concentration of 0.3×10^{-2} M, reduced colloidal iodides in proportion to its concentration, similar to the reaction presented in Reaction (12). In a batch dissolver, where fuel is sheared into the dissolver over a period of time, or in a continuous dissolver where the fuel is added periodically, relatively high concentrations of nitrous are maintained. When the fuel addition stops and fuel dissolution subsides, nitrous acid concentrations will reduce (Sakurai et al., 1995). Therefore, it is only present in solution at elevated temperatures when its production rate exceeds its decomposition rate, as it is unstable at elevated temperatures (Sakurai et al., 1996).

Fig. 5 shows the most commonly expected species in dissolver solutions and their relationship to each other. However, the exact controls on the speciation are poorly understood as are the conditions required to drive the equilibrium toward aqueous iodine, which can then be volatilised to gaseous iodine and captured and treated in the DOG system. In an attempt to understand the experimental parameters that control the removal of iodine from SNF solutions, we investigated the removal of iodine from solution at temperatures representative of dissolver conditions. The experiments were performed in the presence of silver and palladium, the fission products reported to most affect iodine speciation.

2. Experimental

All chemicals used were of analytical grade or better and supplied by Sigma-Aldrich, unless otherwise specified. Stock solutions were prepared using Type 1 water (>18 MΩ/cm) and all iodide solutions were stored in amber bottles to minimise photo-oxidation.

2.1. Simulated dissolver design

The experimental set-up was designed to simulate a SNF dissolver and is shown in Fig. 6. The glass reaction vessel was jacketed to maintain a constant temperature, which was achieved using an external circulating water bath. The vessel was stirred using a magnetic stirrer and a multi-port lid covered the vessel. The lid was constructed of PTFE and contained threaded PTFE connectors, through which all equipment passed and was connected using Rodaviss threaded connectors. The reaction vessel, lid and connectors were all supplied by Radleys. An external cylinder was used to sparge the solution. The inlet gas passed through a needle valve to reduce the gas flow into the reaction vessel. A Liebig condenser was added to the gas outlet to minimise solution losses at elevated temperatures, which in turn was connected to three gas wash bottles. The wash bottles contained aqueous sodium hydroxide (bottle 1, 0.01 M) and aqueous sodium thiosulfate (bottles 2 and 3, 0.01 M) to scrub iodine from the outlet gas flow. An aqueous sampling loop allowed the collection of samples for analysis via ICP-MS. A thermocouple was also present to monitor the temperature of the solution. All tubing was made of either PTFE or 316 stainless steel, with a diameter of ¼ inch. With the exception of the water bath and gas cylinder, all the apparatus was located inside a fume hood.

2.2. Aqueous sample analysis

Aqueous samples were analysed using a PerkinElmer ELAN DRC-e ICP-MS with a S10 autosampler. Due to problems with the analysis of iodine, see below for details, two sets of samples were prepared per analysis point: one set for the analysis of silver and palladium and one set for iodine analysis. Silver and palladium concentrations were determined by suitable dilution into 2% nitric acid, as per standard operating procedures for ICP-MS analysis. The analysis of iodine in diluted nitric acid solutions was challenging and resulted in very poor R^2 values (<0.8) during calibration. Iodine has a high ionisation potential, which results in relatively few iodine ions entering the mass spectrometer (Todorov and Gray, 2016). Additionally, volatilisation can occur during aerosol formation in the nebuliser, causing analyte losses and severe memory effects, which affect the reproducibility of the results. Memory effects occur as a result of iodine compounds being adsorbed on the nebuliser tube surfaces and volatilisation of HI and I_2 from the spray chamber walls (Badocco et al., 2016; Oliveira et al., 2010). This adsorption leads to the random elution of iodine. To overcome these difficulties, iodine analysis was carried out by preparing samples via alkaline extraction using tetramethyl ammonium hydroxide (TMAH) (Oliveira et al., 2010; Boutakhrit and Bolle). A series of calibration standards and solutions of known iodine concentration were prepared in 0.05 M TMAH to test the applicability of this method to our experimental system. The calibration curve resulted in an R^2 value of 0.999 and iodine values within 5% of their expected values. Therefore, calibration standards and samples for iodine analysis from our experiments were prepared by diluting in 0.05 M TMAH. The wash solution was also changed to 0.05 M TMAH.

It should be noted that TMAH is extremely toxic and requires extra precautions while handling. Additionally, the instrument had to be carefully rinsed with DI water when switching between nitric acid and TMAH and back again, due to chemical incompatibility between nitric acid and TMAH.

2.3. Iodine removal experiments

The removal of iodine, in the presence of the fission products silver and palladium, from nitric acid solutions was carried out at two temperatures, 60 and 80 °C. These temperatures were chosen as they represent two of the temperatures reached during different stages of head-end reprocessing, plutonium conditioning at 60 °C and shearing of the fuel at 80 °C (Sakurai et al., 1995). The concentrations of the different species in solution are shown in Table 3, including the concentrations used in our experiments.

A solution containing silver and palladium in nitric acid, at the scaled concentrations presented in Table 3, was placed inside the reaction vessel, which was continuously sparged with air. This solution was allowed to reach the desired temperature before an aliquot of solution containing iodide was added to initiate the reaction. Aqueous samples were removed at various time intervals over 5 h and analysed for iodine, silver and palladium. At the conclusion of the experiment, an aliquot of solution was removed from the gas wash bottles and analysed for iodine.

3. Results and discussion

Figs. 7 and 8 show photographs of the reaction vessel with time at 60 and 80 °C, respectively. At both temperatures, the solutions are initially very dark and opaque, as a result of the colour of the palladium solution. As the experiments proceed, the initially opaque solutions become translucent pale brown, suggesting that a reaction is occurring. As may be expected, the colour change occurs more rapidly at 80 °C than at 60 °C. There is also a visible black ring that formed on the reaction vessel that became more pronounced as the reaction proceeded. It was initially assumed that this was due to the deposition of silver and/or palladium but the ICP-MS results do not support this, as the concentrations of both metals in solution remains similar to the initial value (Fig. 9b and c). More research is needed to identify the composition of the ring.

The concentration of iodine in solution decreases with time (Fig. 9a). The decrease in solution concentration occurs extremely rapidly as within 30 s of the addition of iodide, over 70% and 90% was removed from solution at 60 and 80 °C, respectively. Over the course of the experiment, the amount of iodine removed from solution at both temperatures increases to around 95%. It has been reported that between 93.3 and 98.5% iodide is volatilised to iodine at 100 °C in similar solutions (Sakurai et al., 1989).

Iodine was detected in the gas wash bottles, which were sampled at the conclusion of the experiments. At 60 °C, approximately 5% of the total iodine was detected in bottle 1 (sodium hydroxide) and less than 1% in bottles 2 and 3 (sodium thiosulfate), while at 80 °C, these values increased to 10% and 5% respectively. This suggests that a portion of iodide was removed from solution via volatilisation to iodine.

These experiments were performed in the presence of silver and palladium, two fission products which have been shown to affect the speciation of iodine. The concentrations of silver and palladium are shown in Fig. 9b and c. The concentration of silver and palladium are initially less than that added suggesting that they were rapidly removed from solution possibly through the formation of insoluble colloids with iodide (Sakurai et al., 1996). The concentration of silver and palladium removed from solution does not correlate to the concentration of iodine, suggesting that more than one process is responsible for the removal of silver and palladium from solution, likely involving the precipitation of palladium and silver iodides, the precipitation of palladium oxide and the various reported iodine reactions. As the reaction proceeded, the concentration of silver and palladium increased, approaching the initial concentration added, while the iodine concentration continued to decrease. It has been reported that the colloids of silver and palladium with iodine are partially soluble in hot nitric acid (Sakurai et al., 1996) and it may be that this is responsible for our observed trends. Attempts were made to identify the species in solution, but the presence of palladium made identification via UV–visible spectroscopy impossible as no light could pass through the solutions.

4. Conclusions

The proposed expansion in nuclear power generation to meet future green energy demands requires that the impact to the environment and the human population are minimised. The long half-life of ^{129}I and its contribution to the aerial dose make it one of the most important radionuclides to control. Most iodine is released during dissolution in nitric acid at the head-end of SNF reprocessing. Maximising gaseous iodine release into the DOG system has advantages, reducing the amount that persists beyond dissolution into the rest of the process where it becomes more difficult to abate. While this is captured and treated in the DOG system, a portion remains that should be removed before the SNF is further treated. The species present and the chemical controls on them and their removal is poorly understood. Here we have conducted a series of experiments looking at the removal of aqueous iodine from solutions, as iodide, in simulated simplified SNF solutions. Over 70 and 90% of the added iodide was removed within 30 s at 60 and 80 °C, respectively, rising to around 95% as the reaction was allowed to proceed. Colloidal iodides of silver and palladium may have formed initially but appear to have dissolved with time at both temperatures. However, it is difficult to identify the species in solution and future work is directed at the identification of the iodine species in the solution.

CRediT authorship contribution statement

Sarah E. Pepper: Data curation, Formal analysis, Investigation, Methodology, Project administration, Writing – original draft, Writing – review & editing. **Alastair Baker:** Methodology, Writing – original draft, Writing – review & editing. **Chris J. Maher:** Conceptualization, Methodology, Project administration, Writing – review & editing. **Mike J. Carrott:** Conceptualization, Methodology, Project administration, Writing – review & editing. **Joshua Turner:** Conceptualization, Methodology, Writing – review & editing. **Bruce C. Hanson:** Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the Department for Business, Energy and Industrial Strategy (BEIS) as part of the Advanced Fuel Cycle Programme (AFCP), which is a co-operation agreement between BEIS and the National Nuclear Laboratory (NNL). The University of Leeds was funded by NNL under contract PO1017418. The authors would like to thank Adrian Cunliffe for ICP-MS analysis and our technician Christopher Bulman for running the Leeds Nuclear Laboratory and assisting with the experimental rig installation.

References

Abney, C.W., Nan, Y., Tavlarides, L.L., 2017. X-ray absorption spectroscopy investigation of iodine capture by silver-exchanged mordenite. Ind. Eng. Chem. Res. 56, 4837–4846. https://doi.org/10.1021/acs.iecr.7b00233.

Amachi, S., 2008. Microbial contribution to global iodine cycling: volatilisation, accumulation, reduction, oxidation and sorption of iodine. Microb. Environ. 23, 269–276. https://doi.org/10.1264/jsme2.ME08548.

Badocco, D., Di Marco, V., Piovan, A., Caniato, R., Pastore, P., 2016. A procedure for the quantification of total iodine by inductively coupled plasma mass spectrometry and its application to the determination of iodine in algae sampled in the lagoon of Venice. Anal. Methods 8, 7545–7551. https://doi.org/10.1039/C6AY02204A.

Berry, F.J., Collins, R.D., Parish, R.V., Moore, L.S., 1987. Studies of iodine in nitric acid and of iodine adsorbed into silver-impregnated silica. Inorg. Chim. Acta. 126, 119–124. https://doi.org/10.1016/S0020-1693(00)81251-7.

Boutakhrit, K., Bolle, F.. The determination of iodine in food with the ELAN-DRC-eICP-MS. https://www.perkinelmer.com/Content/applicationnotes/far_iodineinfoodwithelandrc-e.pdf. (Accessed 12 February 2021).

Chameides, W.L., Davis, D.D., 1980. Iodine: its possible role in tropospheric photochemistry. J. Geophys. Res. 85, 7383–7398. https://doi.org/10.1029/JC085iC12p07383.

Chung, H.R., 2014. Iodine and thyroid function. Ann Pediatr Endocrinol Metab 19, 8–12. https://doi.org/10.6065/apem.2014.19.1.8.

Cuevas, C.A., Maffezzoli, N., Corello, J.P., Spolaor, A., Vallelonga, P., Kjaer, H.A., Simonsen, M., Winstrup, M., Vinther, B., Horvat, C., Fernandez, R.P., Kinnison, D., Lamarque, J.-F., Barbante, C., Saiz-Lopez, A., 2018. Rapid increase in atmospheric iodine levels in the North Atlantic since the mid-20th century. Nat. Commun. 9, 1452. https://doi.org/10.1038/s41467-018-03756-1.

Eigen, M., Kustin, K., 1962. Kinetics of halogen hydrolysis. J. Am. Chem. Soc. 84, 1355–1361. https://doi.org/10.1021/ja00867a005.

Energy White Paper: powering our net zero future. https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/945899/201216_BEIS_EWP_Command_Paper_Accessible.pdf. (Accessed 25 October 2021).

Fuge, R., Johnson, C.C., 2015. Iodine and human health, the role of environmental geochemistry and diet, a review. Appl. Geochem. 63, 282–302. https://doi.org/10.1016/j.apgeochem.2015.09.013.

Guido-Garcia, F., Law, G.T.W., Lloyd, J.R., Lythgoe, P., Morris, K., 2015. Bioreduction of iodate in sediment microcosms. Min. Mag. 79, 1343–1351. https://doi.org/10.1180/minmag.2015.079.6.10.

Heikinheimo, J., Kärkelä, T., Tyrpekl, V., Nižňanskỳ, M., Gouëllo, M., Tapper, U., 2021. Iodine release from high-burnup fuel structures: separate-effect tests and simulated fuel pellets for better understanding of iodine behaviour in nuclear fuels. MRS Adv 6, 1026–1031. https://doi.org/10.1557/s43580-021-00175-1.

Hou, X., Hansen, V., Aldahan, A., Possnert, G., Lind, O.C., Lujaniene, G., 2009. A review on speciation of iodine-129 in the environmental and biological samples. Anal. Chim. Acta 632, 181–196. https://doi.org/10.1016/j.aca.2008.11.013.

Hu, Q.H., Moran, J.E., Gan, J.Y., 2012. Sorption, degradation and transport of methyl iodide and other iodine species in geologic media. Appl. Geochem. 27, 774–781. https://doi.org/10.1016/j.apgeochem.2011.12.022.

Hudson, P.I., Buckley, C.P., 1996. Aerial and liquid effluent treatment in BNFL's thermal oxide reprocessing plant (THORP). In: Iguchi, T.T., Fukahori, T. (Eds.), Proceeding of the 1995 Symposium on Nuclear Data. Japan Atomic Energy Institute, pp. 155–176.

IAEA, 2014. Treatment of Radioactive Gaseous Waste. IAEA-TECDOC-1744.

Jubin, R.T., Strachan, D.M., Soelberg, N.R., 2013. Iodine Pathways and Off-Gas Stream Characteristics for Aqueous Reprocessing Plants – A Literature Survey and Assessment. INL/EXT-13-30119.

Kara, P.O., Gunay, E.C., Erdogan, A., 2014. Radioiodine contamination artifacts and unusual patterns of accumulation in whole-body I-131 imaging: a case series (2014). Int. J. Endocrinol. Metabol. 12, e9329. https://doi.org/10.5812/ijem.9329.

Kireev, S.V., Shnyrev, S.L., 2015. Study of molecular iodine, iodate ions, iodide ions and triiodide ions solutions absorption in the UV and visible light spectral bands. Laser Phys. 25, 075602 https://doi.org/10.1088/1054-660X/25/7/075602, 11 pages.

Koenig, T.K., Baidar, S., Campuzano-Jost, P., Cuevas, C.A., Dix, B., Fernandez, R.P., Guo, H., Hall, S.R., Kinnison, D., Nault, B.A., Ullmann, K., Jimenez, J.L., Saiz-Lopez, A., Volkamer, R., 2020. Quantitative detection of iodine in the stratosphere. P Natl Acad Sci USA 117, 1860–1866. https://doi.org/10.1073/pnas.1916828117.

Konings, R.J.M., Wiss, T., Beneš, O., 2015. Predicting material release during a nuclear reactor accident. Nat. Mater. 14, 247–252. https://doi.org/10.1038/nmat4224.

Kulyuknin, S.A., 2012. Fundamental and applied aspects of the chemistry of radioactive iodine in gas and aqueous media. Russ. Chem. Rev. 81, 960–982. https://doi.org/10.1070/RC2012v081n10ABEH004269.

Lengyel, I., Epstein, I.R., Kustin, K., 1993. Kinetics of iodine hydrolysis. Inorg. Chem. 32, 5880–5882. https://doi.org/10.1021/ic00077a036.

Leudet, A., Miquel, P., Goumondy, P.J., Charrier, G., 1983. In: First, M.W. (Ed.), Proceedings of the 17th DOE Nuclear Air Cleaning Conference. Harvard Air Cleaning Lab, Cambridge, MA.

LifeCycle assessment of electricity generation options. https://unece.org/sites/default/files/2021-10/LCA-2.pdf. (Accessed 9 March 2022).

Lin, C.C., Chao, J.H., 2009. In: Preedy, V., Burrow, G., Watson, R. (Eds.), Comprehensive Handbook of Iodine, first ed. Academic Press, Amsterdam.

Maher, C.J., 2015. In: Taylor, R. (Ed.), Reprocessing and Recycling of Spent Nuclear Fuel. Woodhead Publishing, Amsterdam.

Nagy, K., Körtvélyesi, T., Nagypál, I., 2003. Iodine hydrolysis equilibrium. J. Solut. Chem. 32, 385–393. https://doi.org/10.1023/A:1024507310112.

National nuclear Data center. https://www.nndc.bnl.gov/nudat3/. (Accessed 9 March 2022).

Oliveira, A.A., Trevizan, L.C., Nobrega, J.A., 2010. Iodine determination by inductively coupled plasma spectroscopy. Appl. Spectrosc. Rev. 45, 447–473. https://doi.org/10.1080/05704928.2010.502207.

O'Dowd, C.D., Jimenez, J.L., Bahreini, R., Flagan, R.C., Seinfeld, J.H., Hämeri, K., Pirjola, L., Kulmala, M., Jennings, S.G., Hoffmann, T., 2002. Nature 417, 632–636. https://doi.org/10.1038/nature00775.

Palmer, D.A., Ramette, R.W., Mesmer, R.E., 1984a. Potentiometric studies of the thermodynamics of iodine disproportionation from 4 to 209 °C. J. Solut. Chem. 13, 685–697. https://doi.org/10.1007/BF00649009.

Palmer, D.A., Ramette, R.W., Mesmer, R.E., 1984b. Triiodide ion formation equilibrium and activity coefficients in aqueous solution. J. Solut. Chem. 13, 673–683. https://doi.org/10.1007/BF00650374.

Paquette, J., Ford, B.L., 1985. Iodine chemistry in the +1 oxidation state. I. The electronic spectra of OI^-, HOI and H_2OI^+. Can. J. Chem. 63, 2444–2448. https://doi.org/10.1139/v85-404.

Paulilo, A., Dodds, J.M., Milliken, A., Palethorpe, S.J., Lettieri, P., 2020. The environmental impacts of reprocessing used nuclear fuels: a UK case study. Sustain Mater Techno 25, e00186. https://doi.org/10.1016/j.susmat.2020.e00186.

Prados-Roman, C., Cuevas, C.A., Fernandez, R.P., Kinnison, D.E., Lamarque, J.-F., Saiz-Lopez, A., 2015. A negative feedback between anthropogenic ozone pollution and enhanced ocean emissions of iodine. Atmos. Chem. Phys. 15, 2215–2224. https://doi.org/10.5194/acp-15-2215-2015.

Qi-min, D., Zuo-yong, C., Mao-liang, L., 2009. Study of the valence state of iodine in simulated fuel solution of medical isotope production reactor. J. Radioanal. Nucl. Chem. 279, 313–316. https://doi.org/10.1007/s10967-007-7245-5.

Read, K.A., Mahajan, A.S., Carpenter, L.J., Evans, M.J., Faria, B.V.E., Heard, D.E., Hopkins, J.R., Lee, J.D., Moller, S.J., Lewis, A.C., Mendes, L., McQuaid, J.B., Oetjen, H., Saiz-Lopez, A., Pilling, M.J., Plane, J.M.C., 2008. Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean. Nature 453, 1232–1235. https://doi.org/10.1038/nature07035.

Reed, W.A., May, I., Livens, F.R., Charnock, J.M., Jeapes, A.P., Gresley, M., Mitchell, R.M., Knight, P., 2002. XANES fingerprinting of iodine species in solution and speciation of iodine in spent solvent from nuclear fuel reprocessing. J. Anal. Atomic Spectrom. 17, 541–543. https://doi.org/10.1039/B110805K.

Riley, B.J., Vienna, J.D., Strachan, D.M., McCloy, J.S., Jerden Jr., J.L., 2016. Materials and processes for the effective capture and immobilisation of radioiodine: a review. J. Nucl. Mater. 470, 307–326. https://doi.org/10.1016/j.jnucmat.2015.11.038.

Saidy, M., Hocking, W.H., Mouris, J.F., Garcia, P., Carlot, G., Pasquet, B., 2008. Thermal diffusion of iodine in UO_2 and UO_{2+x}. J. Nucl. Mater. 372, 405–415. https://doi.org/10.1016/j.jnucmat.2007.03.272.

Saiz-Lopez, A., Fernandez, R.P., Ordóñez, C., Kinnison, D.E., Gómez-Martin, J.C., Lamarque, J.-F., Tilmes, S., 2014. Iodine chemistry in the troposphere and its effects on ozone. Atmos. Chem. Phys. 14, 13119–13143. https://doi.org/10.5194/acp-14-13119-2014.

Sakurai, T., 1996. Photooxidation of iodine catalysed by uranyl nitrate. J. Nucl. Sci. Technol. 33, 266–267. https://doi.org/10.3327/jnst.33.266.

Sakurai, T., Takahashi, A., Ishikawa, N., Komaki, Y., 1989. The behaviour of iodine in a simulated spent-fuel solution. Nucl. Technol. 85, 206–212. https://doi.org/10.13182/NT89-A34241.

Sakurai, T., Takahashi, A., Ishikawa, N., Komaki, Y., Ohnuki, M., Adachi, T., 1993. Thermochemical and experimental considerations of NOx composition and iodine species in the dissolution of spent PWR-fuel specimens. J. Nucl. Sci. Technol. 30, 533–541. https://doi.org/10.1080/18811248.1993.9734515.

Sakurai, T., Takahashi, A., Ishikawa, N., Komaki, Y., Ohnuki, M., Kato, K., 1995. In: First, M.W. (Ed.), Proceedings of the 23rd DOE/NRC Nuclear Air Cleaning Conference (NUREG/CP-0141, CONF-940738). Harvard Air Cleaning Laboratory, Cambridge, MA.

Sakurai, T., Takahashi, A., Ishikawa, N., Komaki, Y., Ohnuki, M., 1996. Influence of NOx and HNO_2 on iodine quantity in spent-fuel solutions. Nucl. Technol. 116, 319–326. https://doi.org/10.13182/NT96-A35287.

Sakurai, T., Komatsu, K., Takahashi, A., 1997. In: First, M.W. (Ed.), Proceedings of the 24th DOE/NRC Nuclear Air Cleaning Conference (NUREG/CP-0153, CONF-960715). Harvard Air Cleaning Laboratory, Cambridge, MA.

Schmitz, G., 2004. Inorganic reactions of iodine (+1) in acidic solutions. Int. J. Chem. Kinet. 36, 480–493. https://doi.org/10.1002/kin.20020.

Sebők-Nagy, K., Körtvélyesi, T., 2004. Kinetics and mechanism of the hydrolytic disproportionation of iodine. Int. J. Chem. Kinet. 36, 596–602. https://doi.org/10.1002/kin.20033.

Sherwen, T., Evans, M.J., Carpenter, L.J., Andrews, S.J., Lidster, R.T., Dix, B., Koenig, T.K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A.S., Ordóñez, C., 2016a. Iodine's impact on tropospheric oxidants: a global model study in GEOS-Chem. Atmos. Chem. Phys. 16, 1161–1186. https://doi.org/10.5194/acp-16-1161-2016.

Sherwen, T., Schmidt, J.A., Evans, M.J., Carpenter, L.J., Großmann, K., Eastham, S.D., Jacob, D.J., Dix, B., Koenig, T.K., Sinreich, R., Ortega, I., Volkamer, R., Saiz-Lopez, A., Prados-Roman, C., Mahajan, A.S., Ordóñez, C., 2016b. Global impacts of tropospheric halogens (Cl, Br, I) on oxidants and composition in GEOS-Chem. Atmos. Chem. Phys. 16, 12239–12271. https://doi.org/10.5194/acp-16-12239-2016.

Soelberg, N.R., Garn, T.G., Greenhalgh, M.R., Law, J.D., Jubin, R., Strachan, D.M., Thallapally, P.K., 2013. Radioactive iodine and krypton control for nuclear fuel reprocessing facilities. Sci Technol Nucl Ins, 702496. https://doi.org/10.1155/2013/702496, 12 pages.

The Paris Agreement, united nations climate change. In: https://unfccc.int/process-and-meetings/the-paris-agreement/the-paris-agreement. (Accessed 19 August 2021).

Thomas, T.R., Pence, D.T., Hasty, R.A., 1980. The disproportionation of hypoiodous acid. J. Inorg. Nucl. Chem. 42, 183–186. https://doi.org/10.1016/0022-1902(80)80237-5.

Todorov, T., Gray, P.J., 2016. Analysis of iodine in food samples by inductively coupled plasma-mass spectrometry. Food Addit. Contam. 33, 282–290. https://doi.org/10.1080/19440049.2015.1131337.

Truesdale, V.W., Luther, G.W., Greenwood, J.E., 2003. The kinetics of iodine disproportionation: a system of parallel second-order reactions sustained by a multi-species pre-equilibrium. Phys. Chem. Chem. Phys. 5, 3428–3435. https://doi.org/10.1039/B303351A.

Tsukaue, Y., Takimoto, Y., Nakao, G., Yoshida, K., 1994. Effect of NOx on oxidation of triiodide ions. J. Nucl. Sci. Technol. 31, 813–820. https://doi.org/10.1080/18811248.1994.9735227.

Umadevi, K., Mandal, D., 2021. Performance of radio-iodine discharge control methods of nuclear reprocessing plants. J. Environ. Radioact. 234, 106623 https://doi.org/10.1016/j.jenvrad.2021.106623.

Urbanski, E.T., Cooper, B.T., Margerum, D.W., 1997. Disproportionation kinetics of hypoiodous acid as catalysed and suppressed by acetic acid-acetate buffer. Inorg. Chem. 36, 1338–1344. https://doi.org/10.1021/ic960745z.

Wayne, R.P., Poulet, G., Biggs, P., Burrows, J.P., Cox, R.A., Crutzen, P.J., Hayman, G.D., Jenkin, M.E., Le Bras, G., Moortgat, G.K., Platt, U., Schindler, R.N., 1995. Halogen oxides: radicals sources and reservoirs in the laboratory and in the atmosphere. Atmos. Environ. 29, 2677–2881. https://doi.org/10.1016/1352-2310(95)98124-Q.

Whitehead, D.C., 1984. The distribution and transformations of iodine in the environment. Environ. Int. 10, 321–339. https://doi.org/10.1016/0160-4120(84)90139-9.

Wiechert, A.I., Ladshaw, A.P., Moon, J., Abney, C.W., Nan, Y., Choi, S., Liu, J., Tavlarides, L.L., Tsouris, C., Yiacoumi, S., 2020. Capture of iodine from nuclear-fuel-reprocessing-off-gas: influence of aging on a reduced silver mordenite adsorbant after exposure to NO/NO_2. ACS Appl. Mater. Interfaces 12, 49680–49693. https://doi.org/10.1021/acsami.0c15456.

Wren, J.C., Paquette, J., Sunder, S., Ford, B.L., 1986. Iodine chemistry in the +1 oxidation state. II. A Raman and UV-visible spectroscopic study of the disproportionation of hypoiodite in basic solutions. Can. J. Chem. 64, 2284–2296. https://doi.org/10.1139/v86-375.