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## Reassessment of caustic scrubbing for radioiodine capture during UNF processing

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The effective removal of iodine-129 from gaseous emissions during used nuclear fuel processing is critical for minimizing environmental contamination and ensuring environmental regulatory compliance. Recent research has focused on optimizing process air, scrubber conditions, and integrating complementary techniques, such as solid sorbents as a polishing step, to improve iodine capture efficiency. The efficiency of a caustic scrubber is influenced by several factors, such as pH, temperature, gas–liquid contact time, and the presence of oxidants, yet the existing literature tends not to consider how these factors might interact or change in importance with process scaling. This perspective advocates for reconsidering how to mitigate many of these factors, especially in view of the transition from laboratory bench to pilot scale and beyond. This paper reviews the principles, operational parameters, and advancements in caustic aqueous scrubbing for radioiodine mitigation, aims to direct the next scientific pursuit of this technology, and inform environmental decision-making.

## 1. Introduction

Gaseous radionuclides, including radioiodine, are produced as fission products from the splitting of atoms from nuclear fuel. These radionuclides can potentially be released by either fuel recycling – as the fuel is purified or prepared for storage – or otherwise released from the core as a result of a nuclear accident. Iodine-129 ( $^{129}\text{I}$ ) is one such volatile radionuclide of concern because of its long half-life ( $1.57 \times 10^7$  years) and its release into the environment is known to have negative environmental and human health effects.<sup>1</sup> Several studies have revealed its accumulation in target organs of living organisms or its widespread oceanic and terrestrial impacts.<sup>2,3</sup> Thus, in pursuit of radioiodine capture, studies have prompted decades of exploring  $^{129}\text{I}$  reactivity and capture in an effort to preclude its involvement in the environmental cycle.<sup>1</sup>

The US Environmental Protection Agency (EPA)<sup>4</sup> and Nuclear Regulatory Commission (NRC)<sup>5</sup> have prescribed a rigorous abatement strategy for  $^{129}\text{I}$  industrial emissions, whereas other countries do not have such a stringent regulatory responsibility. Recently, the increase in US power demand has renewed interest in modifying regulations due to recent executive orders (EO# 14299–14302). Yet, several scientific challenges to meet regulations remain if the United States were to restart the processing of used nuclear fuel (UNF).

Radiolytic off-gas capture of volatile iodine is particularly elusive and difficult to track, which adds complexity to the development of recommended solutions to iodine abatement.

Examples of the methodologies studied to capture radioiodine include hyperzeotropic nitric acid (IODOX),<sup>6,7</sup> mercury salts,<sup>8,9</sup> chemisorption to solid sorbents,<sup>10,11</sup> and caustic aqueous solutions. The bulk of current research efforts focus on caustic scrubbing,<sup>12,13</sup> and it is the focus of this perspective.

In this perspective, we provide insights driven by the findings and recommendations of the current literature on these topics with a focus on the viability and implementation of caustic aqueous hydroxide scrubbing as an abatement mechanism for capturing radioiodine. In addition, we discuss the possibility of using a higher temperature caustic eutectic salt, that is being considered for radioiodine capture in a molten salt reactor off-gas system.<sup>14</sup>

### 1.1 Influences on radioiodine inventory

The nature and composition of the off-gas produced from used nuclear fuel processing (recycling) is subject to a number of factors, which are often correlated to the amount and presence of  $^{129}\text{I}$ . These factors can include the following:<sup>15</sup>

- Reactor type, the type of fuel used, and neutron flux characteristics. Together, these influence the production of fission and activation products that are to be expected during operations.
- Initial enrichment affects the starting composition of fissile material. This affects the final isotopic spread based on the bias of  $^{235}\text{U}/^{238}\text{U}$ .
- Burnup affects both the overall production of fission products, as well as the potential for more or less transmutation of these fission products.

- As the cooling time after removal from the reactor core increases, the abundance of short-lived radionuclides that are present in the fuel decreases.

- The processing flowsheet of a facility governs the material flows based on which unit operations are being implemented. For example, mechanical or laser shearing may release some of the volatile radionuclides trapped between the inner wall of the cladding and the fuel. Subsequently, dissolution may further release more volatiles as the fuel oxide matrix is degraded, liberating the interstitially sequestered gases. An example schematic of processing unit operations is given in Fig. 1.

In a typical process, fuel rods are cut into pieces prior to entering the dissolver. Once dissolved, the solution is then transferred to the separations tank where it is contacted with an organic phase. The recovered materials are prepared for reuse while the fission products are prepared for long-term storage. Throughout this scheme there are several expected release points for volatile radioactive gases (green) into the process off gas stream. Broadly speaking, irradiation history dictates the composition of the UNF, as do—in the case of flowsheet design—the quantities of radionuclides such as  $^{129}\text{I}$  expected to be present in the incoming gas stream.

## 1.2 Radioiodine liberation

Bruffey *et al.*<sup>16</sup> and Jubin *et al.*<sup>17</sup> tracked the iodine release pathways through the processes that comprise the off-gas of UNF processing, focusing on the potential to trap all potential iodine species. The pathways are summarized in Table 1 and are adapted from a liquid metal fast breeder

reactor report by Goode and Clinton.<sup>18</sup> The main iodine species identified include elemental iodine (principally  $\text{I}_2$ , but also atomic iodine,  $\text{I}$ ),  $\text{CsI}$ , organic iodine compounds (often classified as  $\text{CH}_3\text{I}$ ),  $\text{HI}$ ,  $\text{HOI}$ , and various water-soluble constituents.

To indicate the degree to which the release of a radionuclide—and, consequently, its corresponding dose to an exposed individual—must be reduced, the decontamination factor (DF) is defined as the ratio of the current, unmitigated release to a desired target, typically some fraction of the allowable regulatory limits (eqn (1)).

$$\frac{\text{Release quantity}}{40 \text{ CFR } 190 \text{ Allowable quantity}} = \text{Minimum DF} \quad (1)$$

The head-end processes shown in Table 1 are unlikely to release much iodine except the small amount that has accumulated in the fuel-cladding gap. Most of the iodine will remain in the fuel matrix until it has been dissolved, pulverized, or voloxidized.<sup>19</sup>

## 2. Off-gas regulations, codes, and standards

Limitations on the release of volatile radionuclides from UNF recycling facilities are governed by the United States Environmental Protection Agency as stipulated in 40 CFR 190, where the dose limits for specific organs and for the whole body are enumerated. For example, specific release limits for  $^{85}\text{Kr}$ ,  $^{129}\text{I}$ , and  $^{239}\text{Pu}$  and other alpha-emitting transuranes<sup>20</sup> are presented in curies (Ci) released per gigawatt per year of electrical power produced. Because these limits are tied to the entirety of the fuel cycle rather than dissolution alone, the limits required for a given facility must necessarily be much lower in practice.

### 2.1 40 CFR 190

A verbatim quote from 40 CFR 190 is provided below:

*The annual dose equivalent does not exceed 25 millirems to the whole body, 75 millirems to the thyroid, and 25 millirems to any other organ of any member of the public as the result of exposures to planned discharges of radioactive materials, radon and its daughters excepted, to the general environment from uranium fuel cycle operations and to radiation from these operations.*

40 CFR 190 further stipulates the following:

*The total quantity of radioactive materials entering the general environment from the entire uranium fuel cycle, per gigawatt per y of electrical energy produced by the fuel cycle, contains less than 50 000 curies of  $^{85}\text{Kr}$ , 5 millicuries of  $^{129}\text{I}$ , and 0.5 millicuries combined of  $^{239}\text{Pu}$  and other alpha-emitting transuranic radionuclides with half-lives greater than one year.*

All calculations related to release doses are performed using the EPA-approved CAP-88 code<sup>27,28</sup> for calculating dose

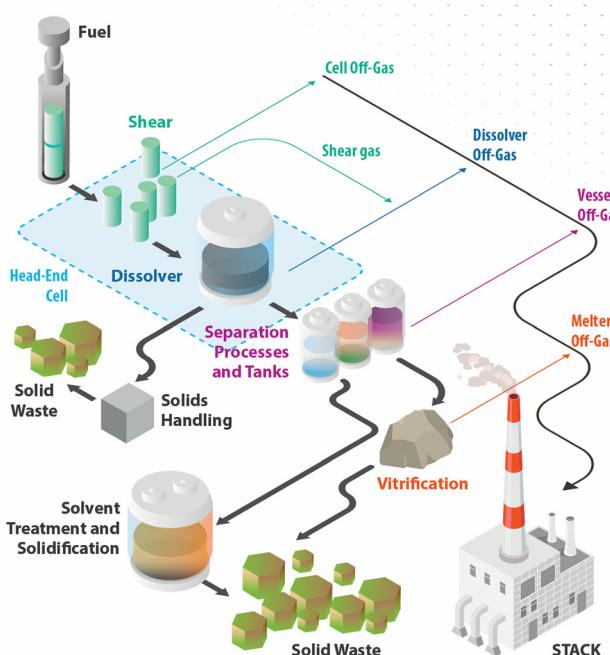


Fig. 1 Schematic of unit operations for an aqueous-based used nuclear fuel processing plant.



**Table 1** Iodine species release pathways in unit operations during processing used nuclear fuel

Process (Fig. 1 representation)	Amount of iodine released	Notes on composition, partitioning	Ref.
Fuel disassembly (not pictured)	Little release (<1%)	I, I <sub>2</sub> , CsI Elemental iodine dissolved in fuel and CsI found at interfaces	21
Shear gas (turquoise arrow)	0.01%	I <sub>2</sub> , DF = 1	17, 22
Dissolver, strong HNO <sub>3</sub> solution (blue vessel)	96% remains in solution. This is a matter of some controversy, with some studies indicating substantial release	DF = 4000 for I <sub>2</sub> , 2000 for penetrating forms <5% converted to penetrating form and released	17
Voloxidation (not pictured, within head-end cell)	Substantial release (>80%)	HI from voloxidation, formed by reaction with tritium	19
Dissolver off-gas (DOG, blue arrow)	0.25%	Released (HI, I <sub>2</sub> , HOI, CH <sub>3</sub> I) Caustic scrubbing did not remove iodine from DOG (only 15%) removed. Organic iodides not very soluble in caustic	23
Dissolver-insoluble iodine (blue vessel)	~3%	PdI <sub>2</sub> and AgI	24
Dissolver leakage (head end cell)	0.07%	I <sub>2</sub> and penetrating, DF = 1	16
Vessel off-gas (purple arrow)	50% of iodine remains in aqueous solution 50% released	10× more flow in the VOG than the DOG stream, 50% organic or penetrating iodine is released. Iodine DF of 1000 and penetrating (organic iodine compounds) DF-500 Off-gas goes to VOG, primarily organic iodides	17
Solvent extraction (multiple vessel unit operation in purple)	70–80% iodine in residual dissolver transfers into organic phase 50% residual iodine released during solvent cleanup with Na <sub>2</sub> CO <sub>3</sub>	Residual iodine species pyrolyzed or incinerated with organic phase – waste off-gas	24, 25
Waste solidification (orange vessel)	0.1–1% of total released, remainder ends up in manufactured waste forms, particulates	Of the small amount of iodine released, 20% I <sub>2</sub> , 10% high molecular weight organic iodides	26

(DF = decontamination factor, which indicates holdup during release. A DF of one indicates that there is no holdup).

at locations some distance from the emission stack. Its outputs are predicated on considerations such as stack height, climate and meteorology, geography, and wind characteristics.

## 2.2 Translating regulations to decontamination factors

It is desirable to apply a level of conservatism over and above that determined by the minimum DF. For instance, the desired DF may be greater than that which is implied by strict adherence to the upper limit set by 40 CFR 190. For example, if the release were determined to be 100 mrem and the approved limit were 25 mrem, then the required minimum DF would be a factor of 4. If the goal were to establish releases that would not exceed even 1/10th of the regulatory limit, the effective DF would be 40. The first clause of 40 CFR 190 is relevant, providing the overall dose allowable to a maximally exposed individual (MEI) from all radionuclides collectively present in the exiting gas stream.

Another key consideration in estimating the required DFs of a given set of radionuclides is the that the list prescribed by 40 CFR 190 is limited. The second clause sets limits for:

- <sup>85</sup>Kr (50 000 curies),
- <sup>129</sup>I (5 millicuries), and
- <sup>239</sup>Pu + all alpha-emitting transuranics with half-lives greater than one year (0.5 millicuries).

Therefore, the extent to which the unspecified radionuclides must be reduced remains at the discretion of the evaluator and is subject only to the constraint that the overall dose level of the gas stream (specified and unspecified) be below 25 mrem and 75 mrem annually to the whole body and thyroid, respectively.

Thus, the evaluator may encounter scenarios in which the curie limits for <sup>85</sup>Kr, <sup>129</sup>I- and <sup>239</sup>Pu, etc. have been met but the resulting total dose exceeds 25 mrem. It is at this point that lower DFs must also be assigned to additional individual radionuclides that contribute to the high dose.

## 2.3 Dose to MEI modelling for aqueous processing of used fuel

The general calculation flow for assessing the dose to the MEI against which the limits in 40 CFR 190 must be measured begins with an accounting of the initial inventory of the radionuclides of interest within the fuel. The corresponding activities of these radionuclides must then be correlated to dose factors to both the thyroid and whole body using the EPA-mandated CAP-88 tool. These radionuclides must additionally be scaled by an appropriate estimate for their release fractions, and, lastly, the annual material throughput or processing rate of the recycling facility in MT/year must be considered (Fig. 2).



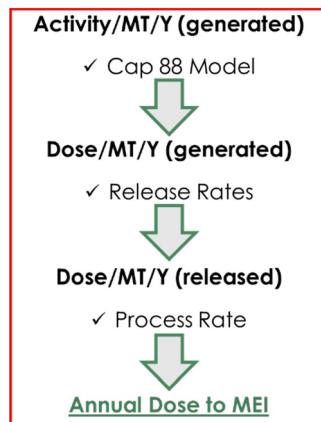


Fig. 2 Workflow illustration to determine overall dose to a maximally exposed individual (MEI).

#### 2.4 CAP-88 relating activity to dose

When estimating the relationship between a given radionuclide and its corresponding dose contribution to both the whole body as well as the thyroid, the CAP-88 software can be utilized to generate the respective dose coefficients (mrem per curie). The dispersion of individual constituents in a plume exiting the stack of a facility may be directional, which is due to the physical characteristics (gaseous *vs.* particulate) of the nuclide, the facility location, and the local meteorology.<sup>29</sup>

In order to minimize the likelihood of skewed results generated by a high-dose radionuclide being dispersed in one direction obscuring the observed dose from a radionuclide being dispersed in another direction, each radionuclide should ideally be specified individually, rather than as a part of a whole fuel inventory. These dose coefficients can then be multiplied by the known activity of each constituent of the fuel to arrive at the associated dose. Table 2 shows example coefficients.

#### 2.5 Release rate considerations

DF estimates should encompass not only the presence of volatilized iodine in the gas stream, but also non-trivial quantities of entrained droplets or particulates. These exist as fluidized and elutriated particles carried by purge and sparge gases present in operations such as dissolution and voloxidation. For example, Herrmann *et al.*<sup>23</sup> performed experiments on a system consisting of a dissolver with a condenser and NO<sub>x</sub> scrubber attached. They observed release fractions on the order of 10<sup>-8</sup>–10<sup>-9</sup> associated with droplets

Table 2 Dose conversion factors. Derived using the EPA approved CAP-88 software tool<sup>27</sup>

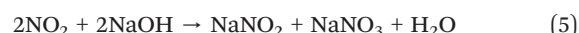
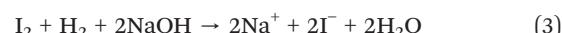
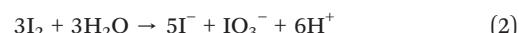
CAP-88 conversion factor (mrem per curie)		
Radionuclide	Total dose	Thyroid dose
<sup>129</sup> I	4.72 × 10 <sup>1</sup>	9.12 × 10 <sup>2</sup>
<sup>85</sup> Kr	8.86 × 10 <sup>-7</sup>	4.37 × 10 <sup>-7</sup>

in the scrubber effluent that contained representative quantities of dissolver solution constituents (Fig. 3).

### 3. Caustic iodine chemistry in liquids

Aqueous hydroxide scrubbing (typically using dilute NaOH) is a well-developed means to capture iodine and acidic gases from a chemical process.<sup>12,30</sup> Because the solubility of iodine species is high in aqueous media, the loading of the off-gas is mostly determined by the chemistry in the condensed phase. However, the solubility depends on pH, redox state, temperature, dissolved metals that can serve as catalysts in iodine equilibria, and the concentration of organic iodides (which will be discussed later).

Caustic scrubbing of I<sub>2</sub> takes place *via* the following chemical equations:



In addition to the advantages of the chemistries above, several advantages of the physical properties of liquid-based scrubbers include (1) good contact between the carrier gas and liquid interfaces, (2) efficient capture and trapping of particulates, mists, aerosols, and potential corrosive/reactive gases (*e.g.*, HF<sub>(g)</sub>, HCl<sub>(g)</sub>, HI<sub>(g)</sub>, F<sub>2(g)</sub>, Cl<sub>2(g)</sub>, NO<sub>2(g)</sub>, and I<sub>2(g)</sub>), and (3) neutralization of acidic species.<sup>31</sup>

When using conventional processing to dissolve UNF with a highly acidic solution, the speciation of iodine will first be in the protonated form of I<sup>-</sup> and I<sub>3</sub><sup>-</sup> forming volatile iodine in the form of HI (H is protium or tritium). Although there has been speculation in the literature that HOI has a long lifetime and will dominate in the gas phase,<sup>32</sup> it has never been definitively measured except in the liquid phase, where it can be detected by reaction with phenol.<sup>33</sup> Insoluble iodine species may also form. Any organic iodides that form in the dissolver will come from impurities in the solution, so their concentration is expected to be very low. The literature suggests that most of the iodine will remain in the dissolver and only about 5% will be converted into a volatile penetrating form (*e.g.* CH<sub>3</sub>I and HI), “penetrating” meaning that it is difficult to trap. About 3% will form insoluble iodides.

From the dissolver, the solution of dissolved fuel and fission products is moved to a series of liquid-liquid extraction vessels (as shown in Fig. 1). When the solution comes into contact with the solvent, a large fraction of the iodine is transferred to the organic phase (up to 80%). Because of the high flow rate of the gas through the vessel (10 times that of the dissolver off-gas), a significant fraction of the iodine is swept up and released

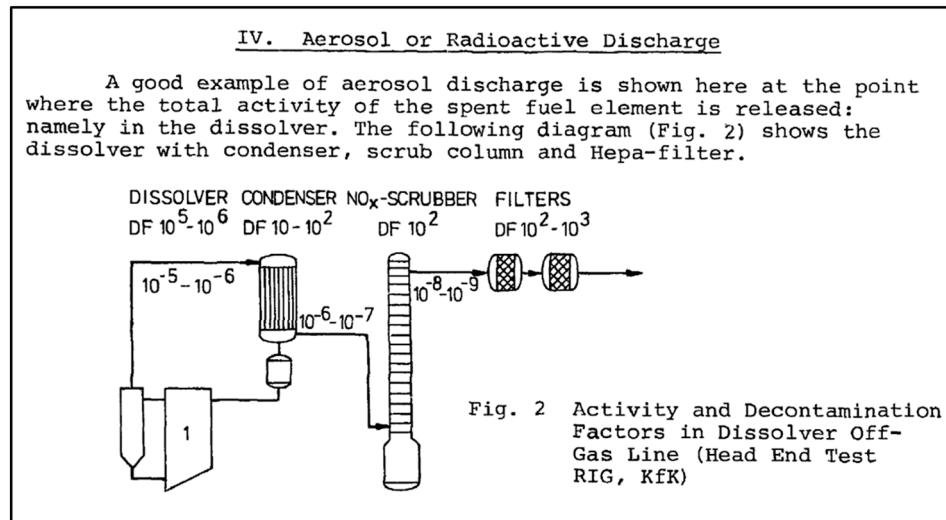
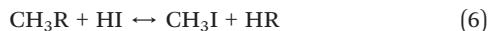


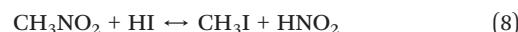
Fig. 3 Diagram from the work of F. J. Herrmann – Harvard Univ., Boston, MA (USA).<sup>23</sup>

to the vessel off-gas (VOG), about 50% of the remaining iodine. Of that fraction, 50% consists of species that are considered difficult to trap, such as organic iodides or HI. The residue from solvent cleanup or incineration of the solvent also releases iodine. The final waste solidification releases only a small fraction of the iodine, less than 1%; of that percentage, 20% is I<sub>2</sub>, and 10% is high-molecular-weight organic iodides. The rest of the iodine remains in the solid waste.

As stated earlier, a significant amount of organic iodide is expected to appear in the off-gas of the VOG, or solvent extraction vessel. One such example, methyl iodide, is water soluble, 14 g/100 mL at 20 °C, but the processes of uptake and removal are both slow. CH<sub>3</sub>R (where R represents an organic moiety introduced during the liquid–liquid separation of dissolved fuel)<sup>2,34</sup> can react with HI or HOI to form CH<sub>3</sub>I as described in eqn (6) and (7).<sup>34,35</sup> Note that the reaction with HI prefers an oxidative atmosphere, and the direct reaction of CH<sub>4</sub> with I<sub>2</sub> is not thermodynamically favored. The presence of I<sub>2</sub> in the aqueous solution or in the solvent can also promote the formation of organic iodides through HI or HOI, depending on the pH.



The presence of NO<sub>2</sub> evolved from nitric acid or added from advanced voloxidation will allow nitrated organics to form, such as CH<sub>3</sub>NO<sub>3</sub> and CH<sub>3</sub>NO<sub>2</sub>. The former is too unstable to have a significant concentration, but CH<sub>3</sub>NO<sub>2</sub> can react with volatile HI to form CH<sub>3</sub>I as shown in eqn (8). CH<sub>3</sub>I, in turn, can react with NO<sub>2</sub> and decompose to regenerate I<sub>2</sub> (eqn (9)). CH<sub>3</sub>NO<sub>2</sub> can also react with CH<sub>3</sub>I to form dimethyl ether and NOI, an unstable compound that will decompose to NO and I<sub>2</sub>.



The kinetics of organic iodide production were explored in great detail by Wren *et al.*<sup>36</sup> via experiments and chemical kinetic modeling. Unlike some off-gas studies, these experiments were undertaken at 90 °C, below the boiling point of water. They found that the release of iodine was greatly dependent on the radiation chemistry that occurs at the water/vessel boundary. Thus, the formation and release of radioiodine depends more on radiolysis that occurs in the liquid phase and damage to materials in contact with the liquid, than to radiolysis of surfaces exposed to the gas phase.

There are many more organic iodides than CH<sub>3</sub>I to be encountered during fuel processing efforts. Wren *et al.*<sup>37</sup> showed that organic iodides can come from reaction of dissolved iodine species with organic materials, paints or epoxies, especially under irradiation. Nakamura *et al.*<sup>38</sup> found that volatile organic iodides, CH<sub>3</sub>I to C<sub>4</sub>H<sub>9</sub>I, will appear in nitric acid, whereas they are not found in other acids. Nitric acid has organic contaminants that can react with radioiodine transported to the dissolver. The larger chain organic iodides are formed by radiolysis, through the generation of organic radicals that can combine to form longer chain organics and organic iodides. Dodecyl iodide, C<sub>12</sub>H<sub>25</sub>I, was found to be prevalent in the radioiodine test facility (RTF).<sup>37</sup> However, these long chain organic iodides are not volatile, and adding organics has been found to reduce the volatility of total iodine.

Methyl iodide has a high vapor pressure (0.053 bar at 25 °C) and can thus be volatilized from aqueous solution.<sup>39</sup> In fuel dissolution, any generated methyl iodide will be difficult to trap. Even in caustic solutions, only a small amount (~15%) has been reported to be captured.<sup>17,23,40</sup>



Therefore, short-chain organic iodides are also considered to be low sorbing or penetrating.

Besides their ease of transport through many of the sorbent beds without being captured, recent sorbent tests reported kinetic inferences from organoiodide sorbing studies. Elemental iodine sorption on solid sorbents occurs markedly slower<sup>11</sup> in the presence of organoiodides, as a function of alkyl chain length. Organic iodides may also poison Ag-based iodine sorbent materials,<sup>19</sup> thus complicating iodine removal from the VOG. For example,  $\text{CH}_3\text{I}$  will be captured by Ag sorbents—forming  $\text{AgI}$  and  $\text{C}_2\text{H}_6$ , but iodine and organoiodide chemistry with other metals, such as copper, are ongoing areas of research.<sup>39,41</sup> Conversely, the formation of large and non-volatile organic iodides has in fact been found to reduce iodine mobility and release.<sup>37</sup> If it is desirable to separate organic iodides and recover the radioiodine for disposal or other applications, then these materials can be heated and oxidized to  $\text{I}_2 + \text{CO}_2 + \text{H}_2\text{O}$ .

The literature further affirms that the fate of organic iodides is not as well understood as inorganic iodides due to the presence of organic iodine in samples close to fuel recycling facilities. For instance, organic iodides have appeared in soil samples collected close to large-scale facilities: at Savannah River in the US, Karlsruhe in Germany,<sup>22,42</sup> and at Sellafield in the United Kingdom.

## 4. Implementation of aqueous hydroxide scrubbing

Caustic scrubbers for radioiodine abatement have been studied since the 1950s at varying test scales (from bench to pilot). Although the chemistry previously discussed favours the capture mechanism, several studies report inconsistent iodine trapping and such irregularity in these studies remains to be understood.<sup>43,44</sup> This section discusses the complexity of iodine behaviour during spent nuclear fuel processing.

### 4.1 Advantages and disadvantages

The advantages of implementing caustic aqueous scrubbing technology for the capture of radioiodine during the recycling of UNF include:

- Hydroxide solutions are inexpensive.
- Scrubber liquids are easily replenishable while in-line.
- Chemistry also favors capture of  $^{14}\text{CO}_2$ .
- Remote handling and maintenance.

Considering these advantages, there appears to be ample opportunity to explore the deployment of this technology for iodine capture. In fact, there are several instances of caustic “wet” scrubbers being used in a variety of other industries—for example, the petrochemical,<sup>45</sup> mining,<sup>46</sup> semiconductor,<sup>47</sup> and pharmaceutical industries.<sup>48</sup>

However, testing of caustic scrubbing with representative fuel processing off-gas streams has revealed several

disadvantages, as mentioned in a NUREG report from 1980,<sup>49</sup> and may include the following:

- Solution sensitivity to acidification (by dissolved  $\text{CO}_2$  or  $\text{NO}_x$  prior to complete abatement).
- Plugging from precipitates (formation of sodium carbonate).
- Difficulty regenerating due to the presence of nitrates/carbonates and therefore requiring intermittent replenishment of caustic solution.
- Low or unpredictable DF (20–90% capture, 2–10 DF).
- Potential for a complex waste form consisting of  $^{129}\text{I}$  and  $^{14}\text{C}$ .

Some instances in early literature report iodine content in caustic waste tank solution with significant variability (test 1 = 17.1%, test 2 = 90%).<sup>50</sup> This reporting was subsequently discussed in a 2005 report, and the authors commented on the effect of acidification and dilution being potential contributing factors to the discrepancies.<sup>44</sup> Furthermore, other methodologies also similarly report large variabilities between tests. For example, several tests implementing an IODOX methodology<sup>7</sup> reported 11–61% removal efficiencies (or DF = 1.5). Unfortunately, we did not find any recent literature that reports an intentional or systematic approach to addressing these discrepancies.

We hypothesize that there could be several contributing factors that have resulted in test inconsistency over the decades. One example is the acidification of the caustic solution due to the co-diffusion of  $\text{NO}_x$  and  $\text{CO}_2$  gases that are known to be present in the process off-gas stream and, thus, decrease the stability of iodine species in the aqueous scrubbing solution. For example, a recent study reports that  $\text{NO}_x$  concentrations do have some influence on scrubber performance if concentrations exceed 5000 ppm.<sup>13</sup> Additionally, due to the lack of real-time monitoring for some tests, it is difficult to predict dynamic behavior and expectations of iodine loading and breakthrough. Radiolysis of iodine in an oxidizing atmosphere has shown that  $\text{IO}_x$  compounds are formed, which have a different behavior than  $\text{I}_2$  or  $\text{HI}$ .<sup>51</sup>

### 4.2 Waste form production

There are several options for preparing caustic solutions impregnated with radioiodine as a waste form, yet all waste forms are subject to additional scrutiny including iodine retention within the matrix and the lack of long-term stability, and feasibility (*i.e.*, if special equipment is required or if it contributes to overall cost). Some strategies to overcome these challenges include testing high-capacity sorbents and stability testing.

Strategies that have been pursued – either from simulated or genuine caustic scrubber solutions – include immobilization into Portland type I/II cement (2.9–4.6 wt%),<sup>9</sup> aluminosilicate materials,<sup>12,52</sup> lead vanadate iodoapatite (6.5–9.4 wt% I),<sup>53</sup> lead zeolites (40 wt%),<sup>54</sup> and bismuth iodates (20 wt%),<sup>55</sup> to name a few.<sup>56,57</sup>



### 4.3 Caustic aqueous scrubber deployment

Caustic aqueous scrubbers have been deployed in the US and at facilities in Europe, Scotland, and Japan in many instances, the details of which are summarized in a different review by Riley and colleagues.<sup>30</sup> Very few studies have employed caustic scrubbing alone; instead, this method has been supplemented with inline sorbent traps or combinations of other iodine capture methodologies. However, it is difficult to find reports on preparing waste forms, perhaps because there are so few repositories being considered. Several reports suggest that radioiodine-containing solutions may be released into the surrounding community seawater,<sup>58</sup> or re-volatilized for capture onto a solid sorbent.

## 5. Opportunities to leverage molten hydroxide scrubbing

An alternative to aqueous caustic scrubbing, is the use of a molten hydroxide salt that can operate at higher temperatures. The properties of such a salt have suggested its application to the decomposition of harmful chemicals such as organo-chlorines as an alternative to incineration<sup>59</sup> or to capture of aryl esters and sulfides generated during coal desulfurization.<sup>60</sup> Molten hydroxides have been proposed for energy applications, such as electrolysis to produce hydrogen gas<sup>61</sup> and for energy storage to increase the utility of renewable resources.<sup>62</sup> Recently, Oak Ridge National Laboratory (ORNL) has developed caustic scrubber design

that uses flowing molten NaOH-KOH for deployment in the off-gas of molten salt reactors (MSRs), including radioiodine species.<sup>26</sup> An example of such a system incorporated into a full system for off-gas management in an MSR is shown in Fig. 4. As with the caustic aqueous scrubber, a molten hydroxide scrubber would be deployed as part of a system with unit operations targeted towards specific fission products or aerosols.

### 5.1 Advantages and disadvantages

The primary advantages conferred by the use of a molten hydroxide system include:

- Greater efficiency is expected through the use of a high surface area packed bed column.
- Lower volume of water introduced into the system.
- Operation at  $>200\text{ }^{\circ}\text{C}$  to handle high decay heat fission products and increase the rate of chemical reactions.
- Remote handling and maintenance.

In regards to iodine trapping, the chemistry of a molten hydroxide scrubber follows similar thermodynamics to a caustic scrubber. Being inherently caustic, a molten hydroxide scrubber could be an advantageous approach to scrubbing acidic gases as well as radioiodine.<sup>64</sup> Additionally, CO<sub>2</sub> and CO would be captured and converted to carbonates in the high temperatures of the molten hydroxide.<sup>65</sup> Tritium could be captured and incorporated in the place of hydrogen of hydroxide (−OH).

The disadvantages of a molten salt eutectic include:

- Purification and handling of hygroscopic salts.
- Materials compatibility.
- Low TRL in all aspects.

When designing a molten NaOH-KOH system, materials compatibility should be taken into consideration due to the chemical and thermal hazards of molten hydroxide. Proper handling and implementation are required to minimize hazards associated with working with molten hydroxide at temperatures up to 300 °C. Ceramics can be corroded by dissolution or by chemical reaction. Corrosion of metals will occur through oxidation or by attack from hydroxyl ions. Corrosion resistant metals, such as Al, are protected by the formation of an oxide film, whereas Ni can exist in thermodynamic equilibrium with the hydroxide indefinitely under a reducing atmosphere.<sup>66</sup> Thus, the materials, equipment, and safety needs for deploying a molten caustic scrubber increases the initial cost of investment, but this method offers an increased capability when compared to conventional aqueous hydroxide scrubbing.

A counterflow packed bed molten hydroxide scrubber design was chosen because it can be drained periodically through a remotely operated valve when the sorption properties of the hydroxide are depleted. In a continuous operation, a second unit needs to be available for a seamless deployment. Alternatively, this could be operated like other standard scrubbers, with continuous small blowdown and makeup stream, however if deployed for an MSR, a blowdown approach

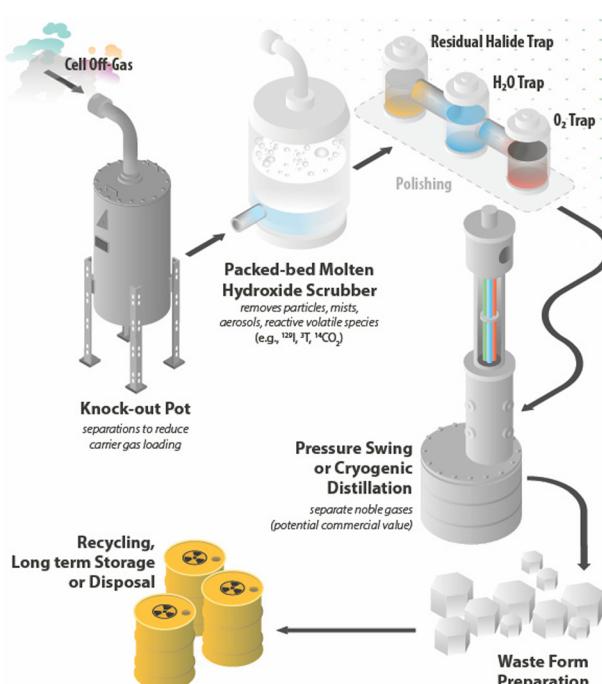


Fig. 4 Schematic of the overall off-gas system for a commercial MSR based on the MSRE experience.<sup>53</sup> All components shown, except the molten hydroxide packed-bed scrubber, are commercially available.



could be problematic both for expense and radionuclide transport. Additional studies to better understand process integration and performance is necessary and expected prior to finalizing and implementing a final design.

Although less water will be liberated from a molten hydroxide, it is expected that the scrubber will release some  $H_2O$  in the form of steam. Thus, it will need to be paired with a series of traps for  $H_2O$ ,  $O_2$ , and perhaps  $I_2$ , the latter being generated from radiolysis within the mixture. As the scrubber itself is not expected to trap  $Xe$  or  $Kr$ , the use of cryogens or novel sorbents (e.g. MOFs) will still be needed.

## 5.2 Scrubber salt selection

Hydroxides are highly hygroscopic and there is considerable literature<sup>68</sup> on how they can be dehydrated, usually involving heating to 450 °C for an extended time (24 h). These salts have a high affinity for  $CO_2$ , forming carbonate, which is not removed by heating. Carbonate is observed even if the salt mixture is prepared under an inert atmosphere as the material supplied from the manufacturer will have some residual contamination. The carbonate is not expected to interfere with iodine capture but may affect the operating conditions over time.

Heat and temperature management in an off-gas system can be a critical consideration in the design of the unit operations. Instead of using pure alkali hydroxides (e.g.,  $NaOH$  or  $KOH$ ), a  $NaOH$ - $KOH$  eutectic (51 mol%  $NaOH$ -49 mol%  $KOH$ ) has a melting point of about 170 °C and was chosen for commissioning the molten hydroxide scrubber at ORNL.<sup>69</sup> Ternary systems  $LiOH$ - $NaOH$ - $KOH$  and other mixtures also have low melting temperatures.<sup>70</sup> Additionally, the boiling temperatures of alkali hydroxide mixtures are quite high, (e.g.,  $Na/K/Li$  2/2/1 is around 1300 °C).<sup>71</sup>

## 5.3 Waste form production

Physical and chemical characteristics of potential iodine waste forms is an active area of research. After cooling, a spent molten hydroxide scrubber would produce a single waste stream as a solid salt and could contain up to 3 of the 4 radioactive off-gas components. Such a strategy is advantageous as it could simplify the off-gas management and potentially the waste form management as well. After removal of high activity fission products, long lived fission products could be secured in a cementitious waste form.<sup>67</sup> Chen and colleagues have investigated the chemistry of iodine *versus* other long lived fission products such as  $Tc$  in synthetic salt stones.<sup>72</sup> The mobility of iodine depends greatly on the pH and redox conditions, as well as the presence of iodine getters, such as  $Ag$  or Friedel's salt.<sup>72</sup>

# 6. Scrubber and facility design considerations

## 6.1 Stack height

The off-gas stack is a structure that facilitates the elevation of the off-gas emissions well above ground level and the heights

of nearby structures. It aids in dispersing the plume of gaseous species by ensuring adequate mixing with the surrounding air. The higher the stack, the higher the plume begins, and the farther downwind the location at which the dispersed plume deposits the residual material. This residual material is thus heavily diluted by the air streams between the stack and the deposition point. From the perspective of the MEI, the reduction of the dose received as a function of increased stack height may be thought of as an implied DF that is dependent on the rate of release and the local meteorological conditions.

Here, the distinction between gaseous volatiles and airborne particulates becomes crucial. Gaseous species may disperse naturally over greater distances, further enhancing their dilution. Particulates may settle and deposit more rapidly, relative to gases. This deposition is also enhanced by precipitation. The increased scrutiny given by 40 CFR 190 to nuclides such as  $^{129}I$  are tied to concerns raised over long-term accumulation in spite of engineering controls such as off-gas stacks.

## 6.2 Facility size

The quantity of volatile radionuclides released from the processing plant scales proportionally with the amount (in tons per year) of fuel processed and its burnup and cooling period prior to processing. From the standpoint of the first clause of 40 CFR 190 cited above, if we assume fixed fractions of volatiles partitioned from the fuel (e.g., 50% of the initial iodine), then as the initial fuel mass increases, so does the released mass of volatiles. However, in light of the second clause, prior to cooling, the volatile fission products are generated proportional to burnup. On a per GW per year basis, this release is thus independent of plant size.

## 6.3 Iodine detection and verification techniques

To monitor the overall efficiency of caustic scrubbing as a unit operation, the development of real-time monitoring of radioiodine is needed to confirm  $^{129}I$  removal from the off-gas. Analytical techniques proposed or implemented for stack detection include laser-induced fluorescence,<sup>73</sup> mass spectrometry (API,<sup>74</sup> APT,<sup>75</sup> and others<sup>76,77</sup>), and gamma spectroscopy.<sup>78</sup>

Intermittent monitoring techniques can also support performance verification and/or detection efforts by sampling from a processing facility. These techniques include liquid scintillation counting,<sup>79</sup> TGA-MS,<sup>80</sup> and ICP-MS/MS,<sup>81</sup> which have either been implemented or studied as viable options for scrubber efficiency monitoring. More recently, a study on leveraging ion chromatography (with method run times of up to 20 minutes) shows promise in quantifying the presence of iodide and iodate from other anions in a caustic solution including chlorides, fluorides, nitrates, nitrites, and carbonates using ion chromatography and UV-vis.<sup>82</sup> A summary by Riley *et al.* provides a synopsis of many available techniques for quantifying iodine.<sup>76</sup>



## 7. Summary

It is vitally important to address the concerns surrounding the liberation of  $^{129}\text{I}$  during nuclear fuel processing and pursue technologies that facilitate its efficient capture. Because of  $^{129}\text{I}$  long-lived radioactivity, its proclivity to accumulate within target organs of living organism, its widespread diffusion water, foodstuffs, and environment it would become vastly more difficult to abate from our natural environment than capture.

Among the many methods that have been proposed as iodine capture unit operations, caustic scrubbing offers the opportunity to provide a simplistic, cheap, and replenishable unit operation. Further, caustic scrubbing of iodine is expected to be chemically favourable. Yet, existing studies which have investigated this method lack cohesion. Scrubber development would benefit from intentional studies to determine (1) the root cause of inconsistent performance and (2) provide reliable insights of the operational bounds can better define caustic scrubbing deployment in a pilot scale facility with radioiodine.

Caustic aqueous scrubbing of refinery gases (*i.e.*,  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  capture from air) has long been deployed in a variety of chemical processing facilities.<sup>83</sup> As such, the implementation of aqueous caustic scrubbing benefits from a higher technology readiness level. However, a molten hydroxide scrubber offers greater efficiency is expected and potential for long-term storage and immobilization of radioactive off-gases. Additionally, molten hydroxide scrubbers also provide unique properties as described above and application challenges in the context of radioiodine mitigation.

This perspective underscores that future studies which target identifying the chemical and physical limitations of caustic scrubbing (molten or aqueous) and their stable waste forms, are extremely important to accelerating the development of the modern fuel processing scheme. These technologies and their practical chemistries appear to be reasonable, and if uncertainties in their operation can be uncovered and bounded, they may prove a viable means to implement radioiodine capture and satisfies the rigor of environmental regulations.

## Author contributions

R. N., J. McF., D. O. and K. R. J. prepared separate sections of this work and provided edits. K. R. J. consolidated the information into a manuscript, prepared its initial submission and revised manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this perspective.

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