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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}I) is one such volatile radionuclide of concern because of its long half-life (1.57×10^7 years) and its release into the environment is known to have negative environmental and human health effects.¹ Several studies have revealed its accumulation in target organs of living organisms or its widespread oceanic and terrestrial impacts.^{2,3} Thus, in pursuit of radioiodine capture, studies have prompted decades of exploring ^{129}I reactivity and capture in an effort to preclude its involvement in the environmental cycle.¹

The US Environmental Protection Agency (EPA)⁴ and Nuclear Regulatory Commission (NRC)⁵ have prescribed a rigorous abatement strategy for ^{129}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 hyperazeotropic nitric acid (IODOX),^{6,7} mercury salts,^{8,9} chemisorption to solid sorbents,^{10,11} and caustic aqueous solutions. The bulk of current research efforts focus on caustic scrubbing,^{12,13} 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.¹⁴

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}I . These factors can include the following:¹⁵

- 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.

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- 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 ¹²⁹I expected to be present in the incoming gas stream.

Bruffey *et al.*¹⁶ and Jubin *et al.*¹⁷ 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

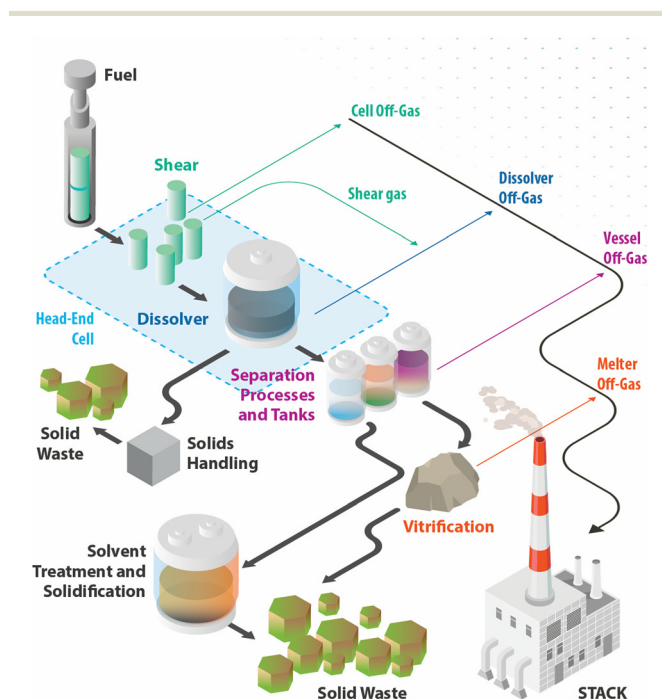


Fig. 1 Schematic of unit operations for an aqueous-based used nuclear fuel processing plant.

reactor report by Goode and Clinton.¹⁸ The main iodine species identified include elemental iodine (principally I₂, but also atomic iodine, I), CsI, organic iodine compounds (often classified as CH₃I), HI, 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.¹⁹

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}Kr , ^{129}I , and ^{239}Pu and other alpha-emitting transuranics²⁰ 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}Kr , 5 millicuries of ^{129}I , and 0.5 millicuries combined of ^{239}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^{27,28} for calculating dose

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 ₂ , CsI Elemental iodine dissolved in fuel and CsI found at interfaces	21
Shear gas (turquoise arrow)	0.01%	I ₂ , DF = 1	17, 22
Dissolver, strong HNO ₃ solution (blue vessel)	96% remains in solution. This is a matter of some controversy, with some studies indicating substantial release	DF = 4000 for I ₂ , 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 ₂ , HOI, CH ₃ 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 ₂ and AgI	24
Dissolver leakage (head end cell)	0.07%	I ₂ 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	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 ₂ CO ₃	Off-gas goes to VOG, primarily organic iodides 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 ₂ , 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:

- ⁸⁵Kr (50 000 curies),
- ¹²⁹I (5 millicuries), and
- ²³⁹Pu + 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 ⁸⁵Kr, ¹²⁹I- and ²³⁹Pu, *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).



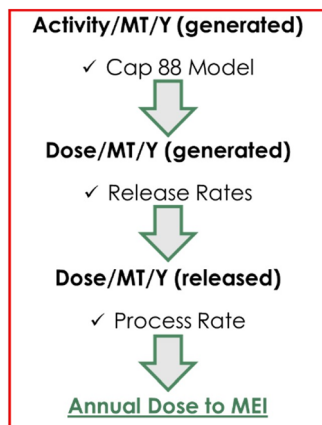


Fig. 2 Workflow illustration to determine overall dose to a maximally exposed individual (MEI).

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.²⁹

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

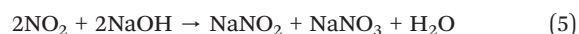
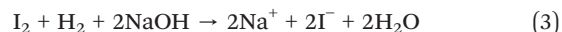
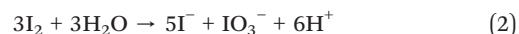
DF estimates should encompass not only the presence of volatilized iodine in the gas stream, but also non-trivial quantities of entrained droplets or particulates. These exist as fluidized and elutriated particles carried by purge and sparge gases present in operations such as dissolution and voloxidation. For example, Herrmann *et al.*²³ performed experiments on a system consisting of a dissolver with a condenser and NO_x scrubber attached. They observed release fractions on the order of 10⁻⁸–10⁻⁹ associated with droplets

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.^{12,30} 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 I₂ 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_(g), HCl_(g), HI_(g), F_{2(g)}, Cl_{2(g)}, NO_{2(g)}, and I_{2(g)}), and (3) neutralization of acidic species.³¹

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⁻ and I₃⁻ 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,³² it has never been definitively measured except in the liquid phase, where it can be detected by reaction with phenol.³³ 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.* CH₃I 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

Table 2 Dose conversion factors. Derived using the EPA approved CAP-88 software tool²⁷

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



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 slower¹¹ in the presence of organoiodides, as a function of alkyl chain length. Organic iodides may also poison Ag-based iodine sorbent materials,¹⁹ thus complicating iodine removal from the VOG. For example, CH₃I will be captured by Ag sorbents—forming AgI and C₂H₆, but iodine and organoiodide chemistry with other metals, such as copper, are ongoing areas of research.^{39,41} Conversely, the formation of large and non-volatile organic iodides has in fact been found to reduce iodine mobility and release.³⁷ 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 I₂ + CO₂ + H₂O.

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,^{22,42} 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.^{43,44} 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,⁴⁵ mining,⁴⁶ semiconductor,⁴⁷ and pharmaceutical industries.⁴⁸

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

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

- Solution sensitivity to acidification (by dissolved CO₂ or 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 ¹²⁹I and ¹⁴C.

Some instances in early literature report iodine content in caustic waste tank solution with significant variability (test 1 = 17.1%, test 2 = 90%).⁵⁰ 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.⁴⁴ Furthermore, other methodologies also similarly report large variabilities between tests. For example, several tests implementing an IODOX methodology⁷ 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 NO_x and 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 NO_x concentrations do have some influence on scrubber performance if concentrations exceed 5000 ppm.¹³ 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 IO_x compounds are formed, which have a different behavior than I_2 or HI .⁵¹

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%),⁹ aluminosilicate materials,^{12,52} lead vanadate iodoapatite (6.5–9.4 wt% I),⁵³ lead zeolites (40 wt%),⁵⁴ and bismuth iodates (20 wt%),⁵⁵ to name a few.^{56,57}

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 cryogenics or novel sorbents (*e.g.* MOFs) will still be needed.

Hydroxides are highly hygroscopic and there is considerable literature⁶⁸ 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 CO₂, 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.⁶⁹ Ternary systems LiOH-NaOH-KOH and other mixtures also have low melting temperatures.⁷⁰ Additionally, the boiling temperatures of alkali hydroxide mixtures are quite high, (*e.g.*, Na/K/Li 2/2/1 is around 1300 °C).⁷¹

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.⁶⁷ Chen and colleagues have investigated the chemistry of iodine *versus* other long lived fission products such as Tc in synthetic salt stones.⁷² 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.⁷²

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,⁷³ mass spectrometry (API,⁷⁴ APT,⁷⁵ and others^{76,77}), and gamma spectroscopy.⁷⁸

Intermittent monitoring techniques can also support performance verification and/or detection efforts by sampling from a processing facility. These techniques include liquid scintillation counting,⁷⁹ TGA-MS,⁸⁰ and ICP-MS/MS,⁸¹ 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.⁸² A summary by Riley *et al.* provides a synopsis of many available techniques for quantifying iodine.⁷⁶



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Author contributions

Conflicts of interest

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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