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Fenton and Fenton-like wet oxidation for degradation and destruction of organic radioactive wastes

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Fenton or Fenton-like oxidation for treatment of organic radioactive wastes is a promising technology with applications to a range of organic wastes. This review details this process; exploring potential challenges, pitfalls and opportunities for industrial usage with radioactive wastes. The application of this process to real radioactive wastes within pilot-plant settings has been documented, with key findings critically assessed in the context of future waste production. Although this oxidation process has not found mainstream success in treatment of radioactive wastes, a lower temperature oxidation system bring certain benefits, specifically for higher volume or problematic organic wastestreams.

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INTRODUCTION

The safe and economical treatment of wastes arising throughout the nuclear fuel cycle is a complex problem due to not only different material characteristics (liquid effluents, organic/inorganic solids, gaseous discharges, etc.) but also the radiological considerations. Routine operation of nuclear power plants, fuel manufacturing, reprocessing, research and decommissioning closed facilities are but some of the few operations liable to generate radioactive wastes. These exist as a wide array of solids, liquids, sludges, ion-exchange resins, etc., which are processed and disposed of according to international and national regulations^{1–3}. These aspects, combined with varying regulatory frameworks across the world do, however, give rise to circumstances in which non-standard treatment technologies can play a key role, especially for small volume or orphan wastes for which construction or utilisation of large-scale conventional processing plants may be economically or technically unjustifiable.

Inorganic wastestreams, although not without their inherent challenges, are often able to be conditioned via existing technologies. This may be vitrification within a glass matrix, solidification via cementation/bituminisation, immobilisation within a ceramic matrix or simply securely encased within a sturdy container if activity levels and chemistry of the waste permit^{3–5}. As such these wastes (and radioactive elements) are typically either chemically incorporated within a durable matrix, or are physically encapsulated by a matrix for which the chemistry and durability is understood. Processing conditions for these materials can be readily tailored to waste compositions. Glasses can be formulated with lower melting temperatures, to avoid volatilisation of certain radionuclides during processing (e.g. caesium or iodine). Different classes of cements can be used to reduce heat output, or vary the internal pH to avoid corrosion/interaction with wastes, and ceramic formulations can be adjusted to incorporate various host elements or impurities^{6,7}.

Organic wastes pose a different challenge to safe waste disposal. Although not typically as highly active as spent fuel or many other higher activity wastes, their organic nature may make them susceptible to degradation over time from heat, radiolysis or

from alkaline conditions (such as cements). This may compromise wasteform integrity, result in chelating organic species or non-aqueous phase liquids, which may enhance radionuclide transport post-disposal, result in a fire risk, or simply be not compatible with existing waste treatment routes designed for inorganic wastestreams⁸. Some organic wastes are more easily categorised and treated than others. Higher volume plastic materials: PVC gloves, wrapping, sample bags, PPE, etc., from known sources, and known chemistries can be routed via nuclearised existing technologies (such as supercompaction or incineration)^{4,9}. More challenging organic wastes, such as organic sludges, animal matter, algae, contaminated oils, etc., may have a more heterogeneous nature, no dedicated waste treatment route, or uncertain provenance.

The wide variety and composition of organic nuclear wastes has led to challenges in materials treatment, and opportunities for alternative treatment processes. One such treatment family is that of advanced wet oxidation, which has at various times found a receptive audience (although not often full commercialisation). The attraction of wet-oxidation processes are typically the promise of a lower temperature decomposition system, which utilises relatively non-toxic materials (metal catalysts, hydrogen peroxide, oxygen), with the output of treated effluents/slurries which can easily integrate into existing waste treatment processes (e.g. on-site liquid effluent decontamination or cementation plants)^{10–12}. A lower temperature aqueous system holds the potential for more simple off-gas requirements, reduced risk of corrosion from high-temperature acids, and a much lower risk of radioelement volatilisation. Coupling this to the potential for large reductions in volume of treated wastes, wet oxidation has drawn continued attention as a technology of interest. Such a system is capable of full operation within a mobile setup, much like a mobile cementation plant or supercompaction system—further adding potential flexibility to this technology^{13,14}.

This review aims to provide a brief overview of current Fenton and Fenton-like wet-oxidation technology, the current scientific understanding, and a deeper look into historical and current applications of this wet-oxidation process to nuclear wastes around the world. Although not currently a technology which has

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found widespread usage within the nuclear industry, this has found niche applications, the lessons from which need to be understood for this technology to have a place within nuclear waste treatment in the future.

FENTON OXIDATION

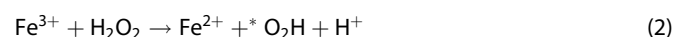
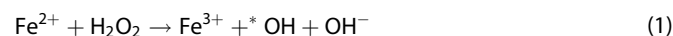
Principles

Fenton oxidation can be classed as an advanced oxidation process, in which H_2O_2 and a source of Fe^{2+} ions are utilised to produce hydroxyl radicals in situ, which go on to decompose organic materials. This reaction was first reported by Fenton in 1894, showing tartaric acid oxidation by ferrous sulphate and H_2O_2 ¹⁵. Since this time, Fe catalysed oxidation has proved to degrade many organic materials, and is the subject of innumerable papers and reviews detailing specific mechanisms.

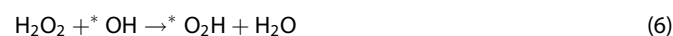
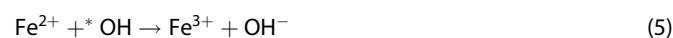
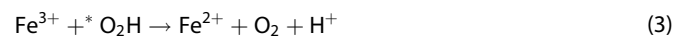
The Fenton reaction utilises $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox with H_2O_2 to produce hydroxyl and hydroperoxyl radicals. The hydroxyl radical possesses an extremely strong oxidation potential, with estimates varying between $\sim 2.0\text{--}2.8 \text{ E}^\circ$ (V), putting the hydroxyl radical between fluorine and ozone among common oxidants^{16–18}. This strong oxidation potential can be exploited to degrade conventionally refractory bio-recalcitrant organic pollutants, such as phenols, pesticides, pharmaceuticals and organic solvents^{10,19}.

The Fenton process is furthermore of great interest due to rapid $\text{Fe}/\text{H}_2\text{O}_2$ reactions, relatively cheap input chemicals, and the ability to progress these reactions at ambient pressure/temperature. Such a system is able to be used as a pre-treatment within existing wastewater treatment plants, and enables the oxidation of organic materials or pollutants to intermediate species, which can be further fully mineralised to non-toxic CO_2 , H_2O and inorganic salts (if inorganic elements are present)^{10,17,20}.

A multitude of studies have been published concerning specific mechanisms within a Fenton reaction, with debate ongoing. The generally agreed upon mechanism of reactions are Eqs. 1–2, in which Fe^{2+} and Fe^{3+} both react with peroxide, cycling to produce radicals, which promote organic degradation. Fe^{2+} acts as the primary catalyst, with regeneration of Fe^{3+} by peroxide. However, regeneration of Fe^{2+} from Fe^{3+} is very slow compared to the main Fe^{2+} reaction, by at least three orders of magnitude^{10,16,17,19,21,22}.



In principle, with an excess of Fe^{2+} and H_2O_2 most organics should be mineralised to CO_2 and H_2O ; however, competitive processes occur which hinder this. While there are many other side reactions, including interactions with organic material which can affect the products and kinetics, some of the most important are Eqs. 3–7, in which the hydroxyl and hydroperoxyl radicals are removed through various mechanisms^{10,16,19,21}.



In these reactions the hydroxyl radical can be scavenged by H_2O_2 , Fe^{2+} and by additional $\cdot\text{OH}$, all of which reduce the efficiency of degradation. Additionally, wastage of peroxide itself can occur due to self-decomposition (especially at higher temperatures)¹⁹. The process is typically rate limited by the presence of Fe^{2+} ions in solution. Regeneration of Fe^{3+} to Fe^{2+} via

Eq. 2 is slower than Eq. 1, and iron can also be lost due to Fe^{3+} ions forming insoluble ferric hydroxide precipitates at circumneutral pH. Consequently, the pH within Fenton reaction process needs careful control, with an optimum pH of $\sim 2.8\text{--}3.0$ where both Fe^{3+} and Fe^{2+} both exist in solution. Unfortunately, at lower pH levels, hydroxyl radicals are increasingly scavenged by protons, and Fe^{2+} decreases—again decreasing the reaction efficiency^{10,19}.

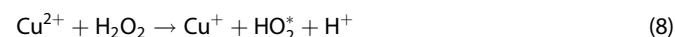
Although Fenton reactions produce strongly oxidising radicals, their high reactivity and low selectivity requires continuous in situ production for organic material degradation¹⁶. This requires a careful balancing of pH, H_2O_2 concentration and supply of Fe^{2+} to maximise the production of hydroxyl radicals, while minimising any terminal reactions which remove these radicals from solution²⁰. Additionally, optimal efficiency of input chemicals is required to reduce costs and minimise secondary effluent streams (e.g. iron hydroxide precipitates).

Modified Fenton-like systems

Improvements and modifications to the traditional Fenton process have been realised with the aim of increasing reaction kinetics, maintaining catalyst reactivity and/or further reduction of remaining organics in treated solutions. Routes to achieving these include usage of alternative homogeneous catalysts, utilising heterogeneous catalysts and using more complex setups such as photo- and electro-Fenton.

Fe catalysts are the most commonly used homogeneous catalyst, being geologically ubiquitous and much less of a pollutant concern than other metals, as well as being the best understood system. Other catalyst elements are available however, with potential for usage of essentially any other element for which multiple oxidation states exist within an aqueous state. This opens up opportunities for oxidation at different pH ranges, potentially affecting wastes in different ways. Catalysts do require careful selection, as problems of toxicity with discharged treated effluents are a risk, if usage of certain elements such as Cu or Cr is encouraged.

Cu is a choice for non-Fe Fenton-like oxidation processes, although acting in a potentially different mechanism to Fe. Alongside a traditional redox system in Eqs. 8 and 9^{10,23}, Walling and Kato proposed that the $\text{Cu}\text{--}\text{H}_2\text{O}_2$ system likely involved organocopper intermediates or ligand transfer, and with potential redox coupling with Fe^{3+} (Eq. 10)²⁴, more recently a wide range of Cu-organic and Cu-inorganic mechanisms have been reviewed²⁵. Cu alone, or in combination with Fe can achieve improved oxidation of materials^{24,26–28}, with the potential for utilisation of copper bearing wastes²³, avoiding further metal additions. One advantage of copper is the apparent wider pH range over which Cu is an active Fenton-like reagent, with particular efficiency closer to neutral pH^{26,29}.



Mn has found some usage as an effective catalyst, particularly when combined with Fe or Cu as a multi-element catalyst^{29–31}. Co (often activated with persulfate) and Ru have also been successfully studied as catalysts¹⁰. The lure of multiple oxidation states over a very wide pH range has drawn researchers to the use of Cr as a Fenton catalyst, finding effective degradation of organic pollutants^{32–34}. Bokare and Choi reported an extensive study of the usage of a $\text{Cr(VI)}/\text{H}_2\text{O}_2$ and combined $\text{Cr(III)–Cr(VI)}/\text{H}_2\text{O}_2$ system for 4-chlorophenol degradation, finding the dual role of H_2O_2 as both an oxidant and reductant for Cr can establish a redox cycle with effective degradation properties^{35,36}—with the option to reduce back to a less toxic Cr(III) after destruction has completed.

Modification of the catalyst physical properties is a variation on the traditional Fenton system, which is increasingly popular. Specifically, instead of a traditional system in which both H_2O_2 and $\text{Fe}^{2+}/\text{Fe}^{3+}$ both exist within solution, a heterogeneous catalyst can be utilised where the catalysing element is solely, or part of a solid matrix, with Fenton reactions largely occurring at the solid–liquid surface interface. Claimed benefits include enabling Fenton reactions to occur at the catalyst surface over a wider pH range, with a lower risk of forming ferric hydroxide sludges, and potentially avoiding the requirement for neutralisation of treated waters^{16,17,37}. The usage of a solid catalyst also enables potential recovery, regeneration (if required) and re-use after (especially with magnetic catalysts), greatly reducing by-products which require disposal.

Fe-based heterogeneous catalysts have been widely explored, with their efficiency governed by many variables, including pH, temperature, Fe oxidation state, surface area and Fe substitution with other cations¹⁷. Iron oxides are among the most well researched, low cost options for heterogeneous catalysis, but research also encompasses iron containing soils, pyrite, goethite, hematite, zerovalent iron, magnetite and engineered iron-silicates^{17,19,21,38,39}. Of these, magnetite (Fe_3O_4) is among the most promising, featuring a spinel structure (AB_2X_4), containing both Fe^{2+} and Fe^{3+} sites. The flexible spinel structure opens up the option of co-doping²⁰. Iron oxides with Co^{2+} , Cu^{2+} , Cr^{2+} and Mn^{2+} in place of Fe^{2+} can increase reactivity^{17,38}. Doping onto the Fe^{3+} site with Cr^{3+} , V^{3+} or elements with a higher charge and similar ionic radii like Ti^{4+} and Nb^{5+} have also shown improvements. These improvements have been proposed to be due to thermodynamically favourable redox pairs ($\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{M}^{n+}/\text{M}^{n+1}$), and the generation of oxygen vacancies, which at the catalyst surface aid in radical production^{20,38,40}.

Other heterogeneous catalysts include clays (often pillared to make them reactive), hydroxalclites intercalated with transition metals (e.g. Cu/Al-LDH), zeolites (e.g. Fe exchanged ZSM-5), transition elements embedded on silica/alumina supports, among others^{16,19,21,41–44}. Cu, Mn, Co and Cr oxide minerals all find usage, although the toxicity of the latter two limits usage other than as minor dopants^{10,25}. Although typically a transition element, a few other elements can find usage as catalysts. Cerium has come to attention due to $\text{Ce}^{3+}/\text{Ce}^{4+}$ cycling⁴⁵. With CeO_2 this forms a peroxide-like species on the surface, limiting reactivity; however, pre-treating with sulphuric acid has shown to create a reactive surface^{10,46}. Aluminium (especially as zerovalent Al) can be utilised, although typically requires a pH lower than 4 or Al_2O_3 can form on the surface, limiting reactivity¹⁰.

Other than varying the catalyst chemistry or physical properties, coupling a Fenton reaction with an external source of UV light (photo-Fenton) has proven to be a popular method for enhancing degradation of various wastes. Typically, either a UV lamp or solar light is utilised to photo-reduce Fe^{3+} to Fe^{2+} , assisting the removal of a bottleneck within the traditional Fenton process. This appears to be particularly effective if degradation products (such as carboxylic acids) form Fe^{3+} complexes^{47–49}. UV radiation can also directly cause photodegradation of organic contaminants, and at wavelengths less than 260 nm can also cause photolysis of H_2O_2 ^{10,16,19}. Although successful, limitations of this method include the extra equipment required to operate, issues with efficiency in heavily polluted waters or due to particulate matter blocking light.

Other less well developed Fenton-like systems exist, typically relying on an additional external source of energy to enhance degradation. Electro-Fenton utilises a potential passed between an anode and cathode, resulting in continuous in situ generation of H_2O_2 and anodic oxidation of organic matter^{10,19,50}. Sono-Fenton harnesses ultrasonic waves to enhance HO^* generation, and creating cavitation bubbles which can assist degradation of pollutants (especially hydrophobic chemicals)^{10,19}. Furthermore

various combinations of the above have been researched, such as sono-photo-Fenton, heterogeneous electro-Fenton, etc⁵¹.

NUCLEAR APPLICATIONS OF WET OXIDATION

Although there are a large body of potential radioactive and toxic wastes, which could be suitable for treatment using a Fenton-like process, open scientific literature studying these wastes is somewhat limited. The bulk of available literature details treatment of ion-exchange resins, with pilot-plant trials undertaken by national institutions, and detailed later per country. As such this section will largely focus on wet oxidation of ion-exchange resins, although available literature for other wastes will be discussed, including that for decontamination liquids and contaminated organic solvents.

Ion-exchange resins

Ion-exchange materials find extensive usage throughout the nuclear fuel cycle, both inorganic materials (e.g. zeolites) and organic resins. Organic ion-exchange resins (IERS) are utilised for controlling radioactivity within nuclear power plants, particularly steam condensate polishing, primary coolant purification, cooling pond activity control and (coupled with organic acids) corrosion/activation product removal. Their specific usage governs the radioactivity within the spent resins, though common radio-nuclides within spent resins include ^{137}Cs , ^{90}Sr , ^{60}Co , ^{59}Fe , ^{54}Mn , ^{14}C and ^3H ^{52,53}. Typically, these resins are granular (or sometimes powdered), highly dispersible material which often require immobilisation per national guidelines prior to disposal.

Many modern routine usage ion-exchange resins for the nuclear industry consist of either strong cation or strong anion resins, with sulfonated (as H^+ , Fig. 1) or quaternary ammonium (as OH^-) functional groups, respectively. These functional groups are usually on a backbone of a crosslinked styrene-divinylbenzene polymer (DVB), with specific crosslinkage and chemistry varying between manufacturers. Although sometimes used separately, many applications of these resins are as a mixed bed of anion/cation resins combined, though targeted applications (such as Cs abatement in cooling pond water) may favour cation selective resins. The quantity of these materials produced, and the

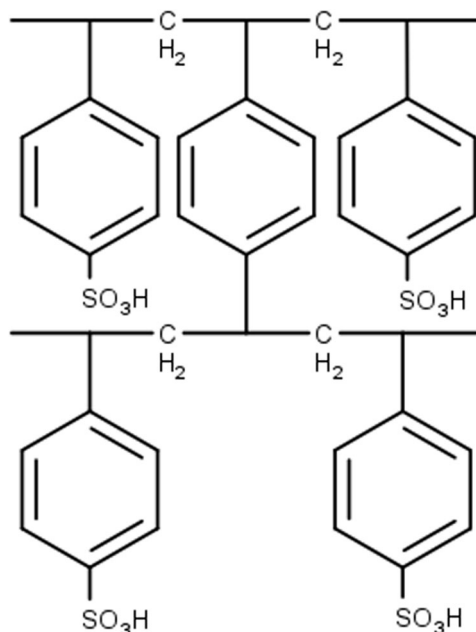
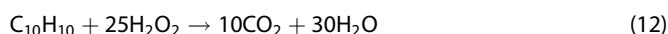
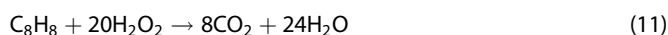


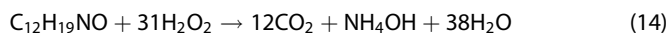
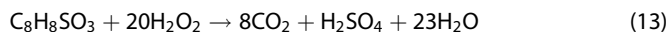
Fig. 1 Structure of a crosslinked polystyrene divinylbenzene ion-exchange resin. Structure shown as sulfonated in H^+ form.

opportunities for substantial volume reduction if treatment is successful has in part driven research into Fenton-like oxidation of spent organic ion-exchange resins.

Overall, the Fenton-like oxidation of organic IERs can be very effective, with reported reductions in organic carbon of >98%, with the capability to just use a source of Fe, H₂O₂ and some pH control. Resulting liquids are normally neutralised, resulting in a sulfate rich product, along with the precipitation of many radionuclides. Shorter treatment times typically result in a higher residual organic content, and a higher presence of lightweight organic species, which appear relatively resistant to Fenton oxidation. The mass balance for wet oxidation of a typical cation styrene-divinylbenzene ion-exchange resin can be split into the oxidation of a styrene monomer (Eq. 11) and a divinylbenzene monomer (Eq. 12), with the degree of crosslinkage formed via additions of DVB within the resin directly affecting H₂O₂ requirements



Functionalisation of resins to form strong cation and strong anionic resins will affect this degradation, Eqs 13 and 14 detail idealised oxidation of a styrene monomer with function sulfate and quaternary ammonium groups, respectively.



Degradation of cationic resins can result in a drop in pH due to release of sulfuric acid (but also due to acidic short chain organic species). Degradation of anionic resins, detailed in Eq. 14, releases alkali species into solution (i.e. NH₄OH), though in the boiling solution this is likely to result in outgassing of ammonia and overall result less effect on pH.

A typical Fenton oxidation setup for wet oxidation of resins consists of a reactor vessel (often glass) into which ion-exchange resins are added. To this both a catalyst and H₂O₂ are added, either initially or slowly over several hours, with the mixture agitated (often magnetically or with forced air bubbling) and the whole vessel heated. A distillation head is typically present in larger studies (and pilot-plant applications), either refluxing condensed liquids back into the reactor, or distilling these into a separate collection vessel. On pilot plants an off-gas system is connected to the system to scrub ammonia and any radionuclides evolved, whereas in laboratory scale these typically exist solely to capture evolved carbon within alkaline traps for quantification. Resins are usually fully solubilised (if not fully mineralised), with inorganic residues precipitating at the bottom of the reactor vessel. Within pilot plants these residues and any supernatant are typically neutralised, with the resultant slurry to be encapsulated (often within a cement).

In general, Fe is utilised with H₂O₂ as an effective catalyst for ion-exchange resin oxidation reactions, particularly for cationic resins^{11,54–57}, with input often as FeSO₄·7H₂O dissolved into a solution to a specific molarity. For anionic or mixed anionic/cationic resins the usage of either Cu or a combined Cu:Fe catalyst has widely been found to be the most effective^{13,54–56,58}—with the usage of Fe alone not producing the lowest chemical oxygen demand (COD) values. Other catalysts have found some usage, with mixed Mn:Cu and Ni:Cu catalysts also effective for anion-resin degradation⁵⁵. A table of key reference papers which tackle IER degradation are listed in Table 1.

The optimum amount of catalyst to add within these reactions is a complicated issue, as results vary by molar strength of catalyst solution, amount of catalyst added to weight of resin, whether the catalyst is added at the start of reaction or continuously throughout (and if added continuously, at what feeding rate),

the ratio of catalysts (if using more than one catalyst), and whether any pre-equilibration was undertaken between the resin and catalysts. This presents a multi-dimensional and interdependent set of reaction variables, with difficulty in recommending an 'ideal' concentration, but certain trends are evident for the multitude of data.

First, pre-equilibration of resins with at least some part of the catalyst solution often results in faster degradation times (especially for cationic resins) and a reduction in foaming observed (notably for anionic samples). Recommended pre-soaking times vary from 15–30 min^{12,58} to 20–24 h^{13,55}. For anionic resins, the addition of citric acid during pre-soaking has been utilised to firstly acidify, and secondly claimed to result in chelated catalyst ions binding to anion-resin functional sites due to anionic metal citrate species^{56,58–60}. These methods are likely to increase Fenton-like reactions occurring at the resin surface, rather than in the bulk liquid, and increase the efficiency of initial resin breakdown. However, due to a risk of catalyst chelation by degradation products, it is sometimes favoured to pre-equilibrate with some catalyst, then continuously feed remaining catalyst throughout the reaction^{12,55}

Strong evidence exists for an optimal concentration of catalyst, with numerous studies finding enhanced dissolution with increasing catalyst concentrations, which hits a maximum before dissolution declines with further increases in catalyst concentration. This could be due to wasteful H₂O₂ decomposition within bulk liquid, rather than at the resin surface with increased catalyst concentrations. For example, Xu et al found a 0.3 M Fe²⁺ catalyst performed better than either 0.1 or 0.5 M catalyst for cationic resins (Fig. 2a)⁵⁷, resulting in earlier resin breakdown and lower final COD values, whereas de Arujano found 50 mM FeSO₄ resulted in more effective degradation than 25 or 100 mM for mixed resins¹². Precise catalyst strength varies greatly, dependant on the amount of catalyst added, specific molarity, quantity of resin, amount of other liquids present, temperature of decomposition and the time of decomposition. The latter of these—time—appears to have a great effect when determining an 'optimum' catalyst concentration. An optimum level of catalyst is often determined by varying molar concentrations of catalyst, running an experiment for a set time, and comparing COD/TOC values of resultant liquors. Often these results show a continued downward trend in COD/TOC values with time—indicating even a suboptimal level of catalyst might result in similar COD/TOC values if experiments were undertaken for slightly longer^{12,58,61}, although with an obvious increase in peroxide usage and time taken to degrade resins. An optimum catalyst also needs to take into account any risks of aggressive reactions, as higher levels of catalyst additions to anion resins in particular have been shown to risk excessive foaming⁶². Further problems occur when trialling 'real' active resins, due to the concentration and variety of metal ions accumulated during operation. Co substituted resins have resulted in lower final COD values than raw resins⁵⁷, while during larger pilot-plant trials the presence of V appears to reduce efficiency, and overall real resins display an increased tendency to foam compared to inactive simulants^{63,64}.

The tendency to froth or foam is not just restricted to active samples. Raw cationic resins degrade relatively easily; however, anionic and mixed cation:anion resins show a marked tendency to froth and foam during degradation^{56,62,65}. The reason for this is not fully understood, although release of ammonia during degradation has been postulated to cause foaming^{62,65}. The dosing of small volumes of organic anti-foaming agents (silicon based, or tri-butyl phosphate) has been successful in reducing foaming^{56,58,62}, as has pre-soaking resins with citric or acetic acid^{58,65}.

The optimum amount of H₂O₂ to add into these reactions is a particularly difficult assessment. Resins are shown to degrade more quickly with faster additions of H₂O₂, with an overall lowest

Table 1. Ion-exchange resin papers (homogeneous).

Ref	Catalyst	Oxidant	Notes (all dark Fenton unless specified)	Waste
Zaharodna et al. ⁶⁷	FeSO ₄ ·7H ₂ O (Fe)	H ₂ O ₂ (15%) Continuous additions	No reflux/condensation 40–60 °C	Cation resin: Amberjet 1500H
Zaharodna et al. ⁶⁸	FeSO ₄ ·7H ₂ O (Fe)	H ₂ O ₂ (15%) Continuous additions	Dark and UV photo-Fenton No reflux/condensation 50 °C	Cation resin: Amberjet 1500H
Gunale et al. ⁷³	CuSO ₄ , FeSO ₄ (Fe, Cu)	H ₂ O ₂ (30%) Batchwise additions	Pre-processing for O ₂ wet oxidation second step 95 °C	Cation resin: INDION-223H
Wan et al. ⁵⁸	CuSO ₄ ·5H ₂ O, FeSO ₄ ·7H ₂ O (Fe, Fe + Cu)	H ₂ O ₂ (30%) Bulk at start	No reflux/condensation 95 °C	Anion resin: Amberlite IRN 78
Xu et al. ⁶¹	CuSO ₄ ·5H ₂ O (Cu)	H ₂ O ₂ (30%) Continuous additions	No reflux/condensation 95 °C	Cation resin: Amberlite IRN 77
Xu et al. ⁵⁷	CuSO ₄ ·5H ₂ O, FeSO ₄ ·7H ₂ O (Fe, Cu)	H ₂ O ₂ (30%) Bulk at start	Vapour condensation outside reactor 60–90 °C	Cation resin: ZG C NR 500
de Araujo and Marumo ¹²	FeSO ₄ ·7H ₂ O (Fe)	H ₂ O ₂ (25%) Continuous additions	No reflux/condensation 40–60 °C	Cation + anion resins: Amberlite IR 120 + Amberlite IRA 410
Feng et al. ⁵⁴	CuSO ₄ ·5H ₂ O, FeSO ₄ ·7H ₂ O, FeCl ₃ , Fe ₂ (SO ₄) ₃ , iron powder (Fe, Cu, Fe + Cu)	H ₂ O ₂ (30%) Continuous additions	No reflux/condensation	Mix of cation and anionic resins: Amberlite IRN 77 + Amberlite IRN 78
Kubota ¹¹	Fe ³⁺ (Fe)	H ₂ O ₂ (9–18%) Bulk at start	No reflux/condensation in main degradation system	Cation: Dowex 50 W X8
Wan et al. ⁶⁶	CuSO ₄ ·5H ₂ O, FeSO ₄ ·7H ₂ O (Fe, Cu, Fe + Cu)	H ₂ O ₂ (30%) Continuous additions	Condensation apparatus on CO ₂ collection system 60–97 °C	Cation: Amberlite IRN 77
Wu and Wu ⁶⁵	CuSO ₄ , FeSO ₄ (Fe—cation only, Cu— anion only)	H ₂ O ₂ (60%) Continuous additions	Influence of varying acids Reflux 97–102 °C Anti-foaming agent	Cation: Purolite NRW-100 Anion: Purolite NRW-400
Feng et al. ⁶⁹	FeSO ₄ ·7H ₂ O (Fe)	H ₂ O ₂ (30%) Continuous additions	UV photo-Fenton 100 °C	Cation: Amberlite IRN 77
Kim et al. ¹⁸⁹	CuCl, FeSO ₄ (Fe, Cu, Fe + Cu)	H ₂ O ₂ (28%) Continuous additions	Electro-Fenton Reflux 80–100 °C	Cation: Amberlite IRN 77
Huang et al. ¹⁹⁰	FeSO ₄ ·7H ₂ O (Fe)	H ₂ O ₂ (50%) Continuous additions	Fluidised bed reactor 75 °C	Cation: Purolite NRW–100

resulting COD when higher total quantities of H₂O₂ are added (e.g. as shown in Fig. 2b)^{11,57,65}. The more quickly H₂O₂ is added, however, the more likelihood of parasitic side-reactions and for H₂O₂ wastage, both not only increasing overall cost but also increasing the volume of resultant liquid effluents. The final acceptable TOC/COD values for a liquid effluent also plays an important role, as driving these values down lower will require more H₂O₂ even after complete resin degradation—with diminishing returns and higher H₂O₂ wastage as TOC/COD values are lowered, especially if the resultant effluent contains a high proportion of difficult to mineralise organic material. This is clearly illustrated in Fig. 3, where continued degradation of resins and associated CO₂ release reaches a crossover point with O₂ release from H₂O₂ breakdown, indicating the increasing wastage of H₂O₂ the longer reactions proceed.

Degradation temperatures play a pivotal role in the efficient degradation of IERs, with utilised temperatures often much higher than many Fenton oxidation studies for conventional wastewaters or pollutants. Degradation of IERs using Fenton-like reactions has

consistently found near-boiling temperatures to produce the most rapid and efficient degradation of resins. Temperatures lower than 90 °C have consistently resulted in higher final COD values, and sometimes incomplete resin degradation^{54,56–58,66}. Helpfully, once initiated, the degradation of IERs is heat-generating, sometimes resulting in self-sustained heating during much of the reaction time⁵⁷—especially for larger industrial-scale setups¹³. Though concerns have been raised that higher temperatures will encourage thermal breakdown and wastage of H₂O₂¹², studies have shown a higher release of O₂ at 83–93 °C compared to 90–99 °C, and a lower CO₂ release at the lower temperatures^{55,56}—emphasising the benefits of higher temperature reactions.

The effect of pH on degradation of IERs is not clear cut. Due to the high organic loading during decomposition of these materials, and the interplay between acidic organic products, sulphuric acid/ammonia generated during decomposition, the pH can alter significantly during degradation. Without altering pH before or during reaction, Jian found cationic resin degradation to result in a

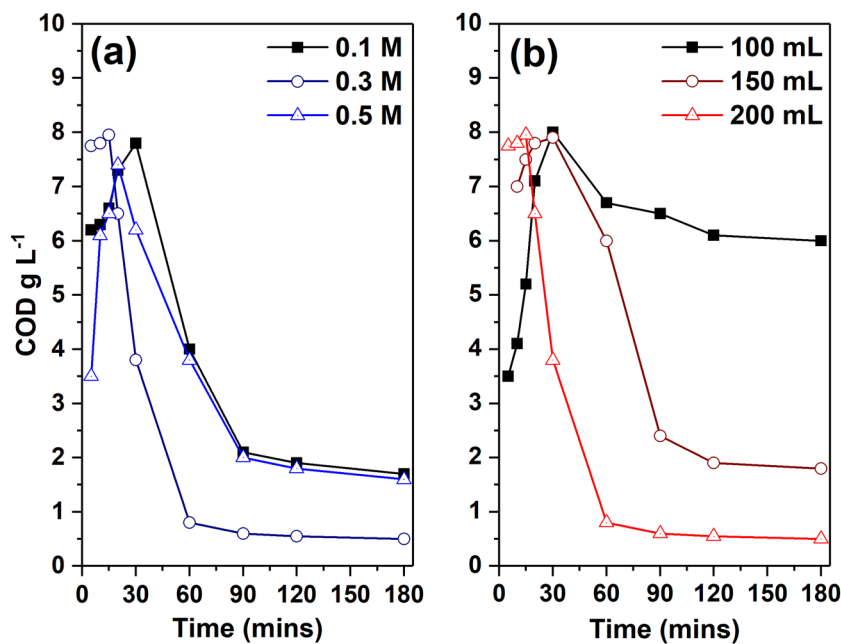


Fig. 2 Varying experimental parameters to enhance degradation. Effect of catalyst (Fe^{2+}) dosage (a), and H_2O_2 additions (b) on IER degradation at 75 °C, adapted from data in Xu et al.⁵⁷. Variables fixed at 75 °C, pH 0.01, 200 mL H_2O_2 addition and 0.3 M Fe^{2+} unless the variable is under investigation.

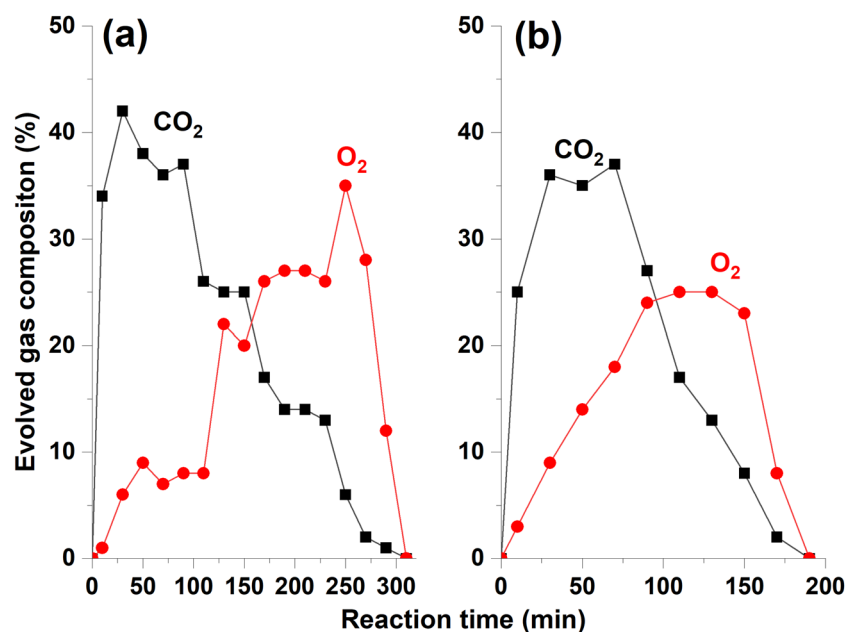


Fig. 3 Variation in gas evolution over time during ion-exchange resin degradation. Release of CO_2 and O_2 measured by Geng et al.⁵⁶ (a) and Jian et al.⁵⁵ (b). Results adapted from sources for comparison.

final liquor pH of 1.0–1.5, anionic resins pH 4.0 and mixed resins pH 2.0⁵⁵ (although Srinivas found cation residual liquids to be pH 2–3, anion resins pH 6–7, and mixed resins pH 2⁶²). Due to the issues with recording accurate pH levels (and constant adjusting) during reactions (near boiling, high turbidity, etc.), many researchers adjust the pH before reactions commence. Some adjust, and find best results at pH 2–3^{54,56,58,67}, others much lower (down to 0.01)^{57,61}, some at circumneutral pH^{12,62}. Feng found initial pH of 2 resulted in highest COD removal, but pH of up to 6 still resulted in >90% COD removal over the same time for cationic resins—with pH of 1, 2 and 3 all performing similarly for anionic resins at 180 min reaction time⁵⁴. Overall the issue of pH

control has not been definitely decided—it seems likely that decomposition of resins impose their own pH regime, although many researchers promote the addition of citric acid to resins (especially anionic resins, but also cationic), which is likely to result in a pH of 2–3^{56,58}.

The destruction of ion-exchange resins is a multi-stage process, likely consisting of varied reactions at ion-exchange sites, destruction of the linear polymer backbone, and oxidation of aromatic components. Once reactions have started, resins are fairly rapidly degraded into soluble products, often with a solution colour change^{56,57}. Degradation of cation resins has been the most studied, with desulfonation of these resins the first step in

oxidative decomposition. A degradation plateau can occur after desulfonation, suggesting complexation of Fe by organic acids inhibiting Fe^{3+} – Fe^{2+} reduction, and thereby limiting further reactions if Fe content is low. Analysis of liquids reveals a wide array of lower molecular weight organics are detected during decomposition, including succinic, maleic, acetic, oxalic and formic acids—along with terephthalic acid from crosslinking⁶⁸. Formic and oxalic acid were the two most abundant degradation products identified, with formic acid predominating at lower catalyst concentrations where dissolution was incomplete, and oxalic acid more prevalent at higher catalyst concentrations after almost complete desulfonation occurred⁶⁸. Feng separately found oxalic, formic, acetic and propionic acids as degradation products (with oxalic acid resistant to further oxidation)⁶⁹.

These degradation products fit well with extensive literature on Fenton oxidation of aromatic substances, particularly phenolic substances, where carboxylic acids are known to be end products^{49,70}. Fe is known to be lost from the system via complexation with these organic acids, affecting redox cycling and reducing achieved mineralisation. Work to improve this includes photo-Fenton to regenerate iron^{47–49}, increasing reaction temperatures beyond 100 °C^{71,72}, or coupling to a high pressure/temperature wet-oxidation system^{73,74}.

The final degradation products from ion-exchange resin treatment usually require disposal or further treatment. A typical homogeneous wet-oxidation setup can result in the formation of iron hydroxide sludges from catalyst precipitation; however, spent ion-exchange resins will also contain various radionuclides, dependant on usage. Resins from fuel cooling ponds will likely contain Cs and Sr, whereas resins for purifying steam turbine water might contain more dissolved metallic ions such as Fe, Ni and Co. Neutralisation of waste liquors can encourage precipitation of some radionuclides as lower soluble hydroxides, with solids and liquors (or partially dewatered solids) immobilised within a cementitious matrix^{12,13,75,76}. Neutralisation is also favoured to enable compatibility with alkali cement powders and ensure a stable product.

The presence of small quantities of these metal hydroxides are unlikely to cause issues for cemented products; however, cation resin degradation results in a high level of sulfate residues left after oxidation. Sulfates will greatly affect the setting characteristics of cements, with sodium and ammonium sulfates known to scavenge Ca to form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), lengthening setting times and deleteriously affecting longer-term strength⁷⁷. If sulfates are neutralised to calcium sulfates, these may also react, as they are known setting regulators in Portland cements. Small quantities of calcium sulfates (gypsum, hemihydrate and anhydrite) are interground during cement manufacture to regulate tricalcium aluminate setting (C_3A , a component of cement clinker), with the complicated interplay (and dosage) of these various sulfates helping to avoid both flash and false setting^{78–80}—addition of calcium sulfates from wastes may upset this balance. Large additions of calcium sulfates can cause later expansive reactions through formation of excessive quantities of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$)⁸¹, although cements blended with high quantities of blast furnace slag are typically more resistant⁸². Certain types of 'supersulfated' cements with very high slag contents make extensive use of calcium sulfates as an integral part of the hardening process^{83,84}, though these are not conventionally utilised materials.

Equally, any residual organic material left after oxidation may interact with cementation reactions, either as free carboxylic acids, or as salts (i.e. oxalic acid or calcium oxalate if neutralised with $\text{Ca}(\text{OH})_2$). Oxalic acid is known to accelerate cement setting and increase the heat of hydration via enhancing alite (C_3S) dissolution from the cement clinker, with precipitation of calcium oxalate monohydrate^{85–87}. Additions of calcium oxalate itself are unlikely to affect cement due to low solubility, but more soluble

organic calcium salts can equally enhance cement setting, such as calcium formate^{88,89}—these could become issues if high levels of organics remain after oxidation.

Decontamination liquid wastes

Chemical decontamination of nuclear facilities (either routine, or post-operational) typically utilises organic chelating agents within an aqueous medium to remove activation products from nuclear facilities (such as those arising from activation of stainless steel/nickel alloys, fuel cladding, etc.), potentially resulting in iron and transition metal rich organic wastestreams⁵³. Depending on the nature of the chelating agent used (e.g. EDTA, citric acid, oxalic acid, picolinic acid, etc.), these may be suitable for wet oxidation, though some, particularly oxalic acid, can be relatively resistant to conventional Fenton oxidation processes.

Direct wet oxidation of organic complexants in radioactive waste has not been widely studied; however, a wide range of literature related to wet oxidation of organic compounds exists for non-radioactive wastes, particularly as many occur as intermediate or final decomposition products of wet oxidation of other pollutants. It is commonly found that low molecular weight acids (LMWA—maleic, oxalic, acetic, formic, etc.) build-up with dark Fenton, affecting final achievable organic mineralisation levels. These and their Fe(III) complexes only weakly react with HO^{\bullet} ⁹⁰, and have been shown to form as decomposition products from a wide range of compounds including (and not limited to) phenol^{49,91,92}, nitrophenol⁷⁰, ethylene glycol⁹³, sawmill wastewater⁹⁴, H-acid⁹⁵ and ion-exchange resins^{68,96}.

Various improvements have been sought to enhance the degradation of these acids. They can be almost completely mineralised with a photo-Fenton process^{47,49,68,70,90–93,97} or solar electro-Fenton process⁹⁸, forming only as intermediate compounds during reactions. Research into oxalate and other LMWAs has also been spurred by their utilisation to improve the photo-Fenton process, (e.g. via Fe(III)-oxalate reduction to Fe(II) under specific UV/light irradiation), including extension of photo-Fenton to more neutral pH ranges^{48,99–101}. Another route to increase degradation has been to increase reaction temperatures. Although not as reactive to dark-Fenton processes, LMWAs can be more readily degraded with an increase in temperature towards 70–90 °C^{42,71}, with even better mineralisation if able to reach 120–130 °C^{71,102}. Equally, different catalysts can also have an effect on LMWA degradation, with most research being undertaken using Fe catalysts. Research suggests Cu(II)-carboxylate complexes are more easily attacked, accelerating mineralisation^{23,98,103}. Mixed Fe–Cu–Mn catalysts have shown good results over a range of organic acids, with Mn performing particularly well with oxalic acid, especially when coupled with elevated temperature^{31,104}.

Less studied is degradation of EDTA; however, this appears to be capable of at least partial mineralisation utilising both conventional and hetero-, photo- and sono-Fenton process, including with recovery of complexed elements (i.e. Ti, Ni, Co) from the resulting treated water^{47,105–110}. This has been particularly demonstrated via the removal of radioactive ⁶⁰Co from EDTA solutions utilising a heterogeneous Fenton reaction with an iron-silicate catalyst³⁹.

Research on simulant and real radioactive waste effluents containing organic acids and chelating agents generally result in high levels of organic destruction^{13,111–115}. Utilising a combined Fe–Cu catalyst, JGC claim 97–100% decomposition of EDTA, formic, citric and oxalic acid at temperatures up to 100 °C¹¹⁴. Lower levels of mineralisation (although still >80%) have been reported for dark-Fenton trials by KAERI for oxalic acid, ascorbic acid and EDTA decontamination solutions, utilising an Fe catalyst at 90 °C¹¹⁵. This system was improved with the addition of a UV-TiO₂ system post-treatment, greatly reducing residual organic contents¹¹⁵.

Contaminated solvents

Fenton processing of radioactive solvents and co-occurring chemicals typically fall into two categories: treatment of research/medical/industry solvents, or treatment of spent nuclear fuel reprocessing solvents.

The former of these: non-reprocessing solvents, includes a wide range of organic materials such as toluene, acetone, liquid scintillation cocktails, chlorinated solvents, etc. These are often complex mixtures from a variety of sources. There have been several trials utilising scintillation wastes^{13,116}, toluene¹¹⁶, acetone¹¹⁶ and chlorinated solvents mixed with oils (with biodegradation after to destroy oil)¹¹⁷. High levels of carbon reduction have been claimed, though increasing volatility with higher temperature processing affected toluene degradation¹¹⁶.

Destruction of spent nuclear fuel reprocessing solvents has been subject to more extensive research. Typically, the wastes are a combination of a solvent (tri-butyl phosphate (TBP), dibutylphosphate (HDPB), tricaprlyl amine (TAA), tri-n-octylamine (TAA)) and either kerosene (OK), n-dodecane, or other alkyl aromatic hydrocarbons. Techniques for treating these consist of either treating as a whole^{118–121}, or initial distillation to remove less reactive hydrocarbons prior to Fenton reaction^{76,122}. Some research has been undertaken on removal of TBP from waste-waters containing surfactants¹²³.

Overall Fenton oxidation is capable of successfully destroying the solvents TBP, HDPB, TCA and TAA at temperatures ~100 °C, typically with an iron catalyst^{118–122,124}, though a chromium catalyst has been trialled¹²⁵. TBP degradation results in decomposition to CO₂, inorganic phosphates (postulated as iron phosphate), and phosphoric acid^{118,119}. Degradation of combined TBP/OK has reported to result in the formation of acetic acid, n-hexadecanoic acid, small amounts of formic acid, and other minor organics. More volatile species are found in condensate liquid, including phosphoric acid, acetone, butanal and acetaldehyde¹¹⁹—other researchers have also found some oil/TBP carried over from the reaction solution¹²¹. Kerosene and n-dodecane often remains atop the reaction solution, with little reactivity, even if well emulsified¹¹⁸.

No widespread treatment of any solvent wastes with Fenton oxidation is currently operational; however, Italian researchers undertook pilot-plant trials for spent reprocessing solvent destruction, described in more detail within the country specific sections.

Other wastes

A few other radioactive wastes have been trialled for Fenton oxidation. Cellulose wastes, in the form of contaminated protective clothing¹²⁶, filter aids/precoats^{127,128} and paper—although often co-mixed with other wastes¹³. Small-scale pilot trials treating mixed organic ion-exchange resins and cellulosic filter aids have been successful^{127,128}. Laundry waste from a Finnish nuclear power plant were also trialled for Fenton treatment. These wastes contain organic surfactants, along with associated radioactivity. Utilising a dark-Fenton process up to 70% COD/TOC reduction was possible¹²⁹.

NUCLEAR APPLICATIONS—PILOT-PLANTS AND INSTITUTIONAL TRIALS

Outside of academic research, several national nuclear research institutions and companies around the world have trialled larger-scale applications of Fenton processes to specific nuclear wastes. This has resulted in several pilot and small-scale plants utilising Fenton chemistry being commissioned, all using homogeneous catalysis. Substantial interest was garnered from the 1980s through to the 2000s, with strong interest from Sweden, Italy, UK, USA and Japan. Overall none of these trialled systems appears to have entered full commercial operation outside of limited testing, although significant experience and knowledge has been acquired from these research programmes.

Sweden

One of the earliest Fenton wet-oxidation plants mentioned in open literature was the ASEA-ATOM/Vattenfall pilot plant in Sweden, operating in the 1980s⁷⁵. This consisted of a pilot plant at 50% scale, capable of handling 100 kg of waste at a time, with a focus on spent ion-exchange resin treatment resulting from commercial operation of light water reactors. The plant implemented a conventional homogeneous Fenton system, utilising sulphuric acid to lower pH, heating to 90 °C, adding a ferrous sulfate catalyst, and continuously applying H₂O₂ over a 5 h reaction time (at least during cold testing). Details of experimental conditions discussed in their patent are in Table 2.

In addition to cold tests, several different active wastes were trialled. These comprised Cs/Sr selective IER media from the Forsmark nuclear power plant (treated successfully with no detected radioactivity carryover to off-gas system), and resins from the startup of the Italian Caorso BWR nuclear power plant.

Table 2. Summary of experiments undertaken by ASEA-ATOM and ENEA.

	Waste	Active	Oxidant	Catalyst	pH	Temp	Duration
<i>ASEA-ATOM</i>							
^{130,131}	IERs (100–500 g L ⁻¹ water)	N	H ₂ O ₂ (50%) 25–50 g kg ⁻¹ IER Continuous addition	Fe ³⁺ (sulfate, nitrate, or acetate) 5–20 g kg ⁻¹ IER	Initial 2 using H ₂ SO ₄	100 °C	'some hours'
<i>ENEA</i>							
⁷⁶	Simulant reprocessing waste	N	H ₂ O ₂ (40%) 18–25 kg L ⁻¹ organic waste	FeSO ₄ ·7H ₂ O 20 g L ⁻¹ waste	–	–	–
⁷⁶	Active reprocessing waste (100 mL)	Y	H ₂ O ₂ (40%) 100 mL h ⁻¹ (cont feed)	Ferrous sulfate 20 g L ⁻¹	–	100 °C	–
¹²⁰	Simulant solvent waste (5 L)	N	H ₂ O ₂ (36%) 55 L @ max 10 L h ⁻¹	FeSO ₄ ·7H ₂ O 100 g each cycle × 3 cycles	addition of H ₂ SO ₄	100 °C	–
¹¹⁸	TBP-n-dodecane mix	N	H ₂ O ₂ (36%) Varying ratios of organic to H ₂ O ₂ 2–30 mL h ⁻¹	Varying catalysts: None, CuO–Cu ₂ O, Pt–C, FeCl ₃	–	–	–
¹¹⁸	n-dodecane	N	H ₂ O ₂ (36%)	FeSO ₄ ·7H ₂ O	–	–	–

The latter waste comprised 10 × 200 L drums of resin, resulting in 1 drum of treated, cemented product. Post-treatment, the resultant liquor has its pH raised to 9.5–11 with either NaOH, KOH or NH₄OH, resulting in precipitation of the poorly soluble transition metal hydroxides, which comprise the core of the radioactivity within these resins^{130,131}. This leaves a sulfate rich supernatant, along with radio-caesium and strontium, which requires disposal. The disposal solution was to either add excess of non-radioactive strontium or barium (SrSO₄/BaSO₄ solubility is limited, an excess of Sr/Ba would likely coprecipitate radio-strontium as a sulfate, removing it from solution), or to elute this supernatant through Cs/Sr selective IER. This was claimed to only use a small capacity of the IER resin, resulting in only minor additional wastes^{75,130,131}. The resulting waste residues were immobilised within a cement, with a claim of high volume reduction compared to conventional cementation of Swedish nuclear power plant resins, with a proposed volume reduction of a factor of 15⁷⁵.

Italy

The problem of spent ion-exchange treatment spurred Italy into developing wet oxidation from the late 1980s. Spent IERs consisted a large fraction of radioactive wastes from NPPs in Italy, with a BWR plant (Montalto di Castro NPP) scheduled to come online in 1988. Due to disappointment with direct cementation of resins, the option of wet oxidation was explored for volume reduction¹³². An added advantage was the option to re-treat spent IERs from the Caorso NPP. Those resins were partially treated with a urea-formaldehyde process, which by 1987 were unable to conform to incoming regulations, with re-conditioning required. To realise this goal, an industrial development program was funded by ENEA's Industrial Promotion Programme (with FBM-Hudson Italiana as industrial partners) from 1985. A pilot plant was envisaged, operating up to 100 kg dry resin in each batch, at the cost of 6000 million Lire (US\$ 4.5 million), with a startup of 1990 planned¹³². Construction of demonstration plants due in this programme (for 1987) were deferred due to the Chernobyl accident, and the programme does not appear to have been restarted.

In 1989 ENEA looked again at wet oxidation, undertaking several studies into the destruction of other organic materials, including olive processing wastes, atrazine, PCBs and solvent wastes, to determine if this treatment method might find application for additional wastestreams in Italy^{118,120,133}. These studies led onto inactive and active trials of homogeneous wet oxidation for the destruction of waste reprocessing solvents, for which a disposal route had not been decided. This waste resulted from the EUREX pilot nuclear reprocessing facility at Saluggia in Italy, which operated from 1970–1983, during which 600 materials testing reactor elements from national research reactors, and 1.5 tonnes of irradiated CANDU fuel were reprocessed^{134,135}. After closure of this facility, 25 m³ of spent reprocessing solvents required disposal, comprising a mixture of tri-butyl phosphate, tricaprilyl amine, kerosene and various alkyl-benzene isomers^{76,122}.

ENEA noted that incineration of these wastes would be challenging due to corrosion from phosphoric acid resulting from tri-butyl phosphate destruction, a problem which had stimulated research into alternative disposal process across Europe. At that time, various alternative technologies existed for the treatment of similar wastes, including the EuroWatt Process (BE) for pyrolysis, and the Silver II electrochemical process undertaken at Dounreay (UK). ENEA decided to trial a multi-stage process of distillation, followed by wet oxidation, coupled with incineration and cementation⁷⁶. As the distribution of radionuclides was not homogeneous within these mixtures, distillation would allow the re-routing of low contamination kerosene to conventional incineration, with contaminated remaining solvents undergoing

wet oxidation, and cement encapsulation of the residues from this process to form a disposable product. Hot distillation trials using 5 L of real solvent material (total α/β: 900–950 kBq L⁻¹, total γ: 222 kBq L⁻¹) were successful, resulting in the majority of activity remaining in solvent waste / residue—rather than in the distillate (allowing for distillate incineration)^{76,122}.

Benchtop wet-oxidation trials began with inactive simulant material, resulting in >95% organic removal with an iron catalysed system (FeSO₄ + H₂O₂), although with a high TOC remaining in the aqueous distillate. The researchers noted that vigorous stirring is necessary, and that 2–3% of the initial volume remains as a viscous unreactive residue after treatment^{76,136}. Post-treatment waste solutions were neutralised with NaOH, followed by addition of Ca(OH)₂ to precipitate sulphates and phosphates. Cement powder was added to the solutions, and rapidly solidified (in a few minutes). Benchtop active trials followed in three batches, using 100 mL real waste each. In this setup, the distillate was condensed, with the aqueous phased collected, and the organic phase recirculated to the reactor. Mixing was undertaken using N₂ bubbling, though this did not result in vigorous mixing, and was believed to affect the final result of only 80% organic removal^{76,136}. A summary of experimental conditions for these, and previous trials are noted in Table 2.

A full-scale treatment plant was planned, utilising the same reactor for both distillation and later wet oxidation (plant scheme shown in Fig. 4). The overall proposed mass balance for the EUREX waste was 25 m³, distilled to 3 m³ of organic residue (for wet oxidation) and 22 m³ organic distillate (mostly kerosene, trimethylbenzenes and some small percentage of TBP, for incineration). Wet oxidation would result in 6 m³ aqueous residue (containing almost all the activity, for cementation), <150 L viscous organic residue, ~50 m³ aqueous distillate, and a yet to be determined volume of scrubbing solution from off-gas treatment⁷⁶. Plans for a plant were described, although it does not appear that the wet oxidation programme progressed further than these hot benchtop trials.

UK

The UK has over the years been one of the more enthusiastic proponents of wet oxidation. Research into application of this to UK wastes has taken two paths—a chromium catalysed system for destruction of waste alkyl phosphate (e.g. tri-butyl phosphate (TBP)) from fuel reprocessing, and a more conventional iron catalysed system for spent ion-exchange destruction, the latter of which has resulted in various research programmes and pilot plants over several decades.

Research into a Cr catalysed system is first recorded in a patent granted to Interox in 1988, detailing the usage of hydrogen peroxide and sodium/potassium chromate for destruction of alkyl phosphates mixed with hydrocarbons (TBP in OK (odourless kerosene) is one example detailed), operating at slightly lower temperatures (65–75 °C), below the flash point of the hydrocarbon solvent¹²⁵. This was claimed to only degrade a small amount of the hydrocarbon, allowing incineration afterwards. A range of catalysts were tested, including Fe, Cu, V, Co, W, Mo, Ru, Mn and Cr, with Cr showing superior performance. With pH control to 7.0 the authors claim 99% TBP destruction with usage of K₂CrO₄, with a small-scale active test retaining 99% of radioactivity within the aqueous phase¹²⁵.

British Nuclear Fuels Limited (BNFL) also similarly undertook research on alkyl phosphate degradation with a chromium Fenton-like process, following the cessation of sea discharge of waste reprocessing solvents in 1983¹³⁷. This culminated in two patents in 1992 and 1996 which utilise a chromium catalyst, but claim various claimed improvements. The first utilises NaOH to hydrolyse the alkyl phosphate, before decanting the hydrocarbon solvent (reducing fire hazards—peroxide and hydrocarbons

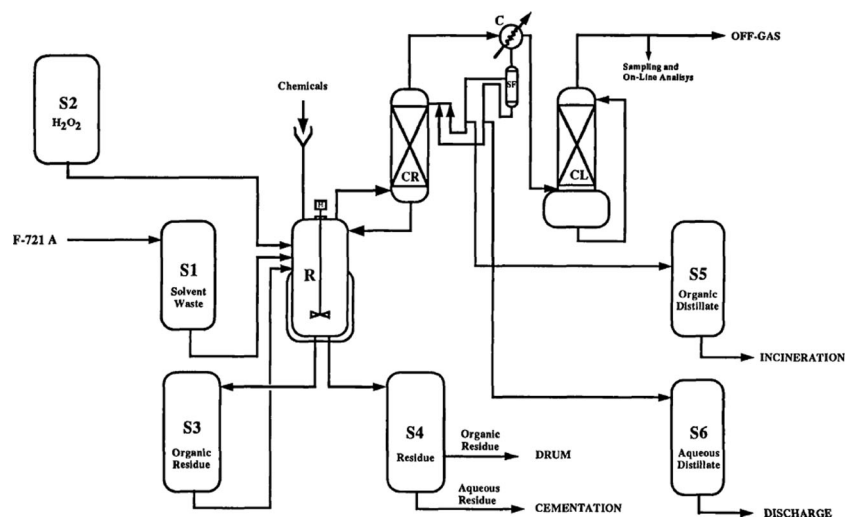


Fig. 4 Simplified plant scheme for ENEA distillation/wet-oxidation system⁷⁶. Fig. notations: R—reboiler for distillation and reactor for wet-oxidation. CR—packed column for distillation. C—condenser. SR—phase separator to allow recirculation of various liquids. CL—washing column for off-gas. S1—waste feed tank. S2—H₂O₂ storage tank. S3—organic residue tank (interim waiting for wet oxidation). S4—aqueous residue tank (interim from wet-oxidation, awaiting cementation). S5—organic distillate interim storage (for incineration). S6—aqueous distillate interim storage (for discharge). Reproduced with permission from ref. ⁷⁶, copyright (EC, 1995).

boiling together were not deemed to be acceptably safe)¹³⁸. The sodium alkyl phosphate is then oxidised with peroxide and a combined Cr + Cu catalyst (combined Cr with V or Fe are also suggested, but not as effective) at circumneutral pH. The second patent applies the chromium/peroxide oxidation process to organic complexants in aqueous solution (e.g. EDTA and citric acid) and BUTEX reprocessing solvent, with a suggestion that Cr could be converted to Cr(III) and precipitated after post-processing to avoid environmental discharge¹³⁹. None of these processes found widespread usage in treatment of waste reprocessing solvents, with further research into wet oxidation in the UK focussing on volume reduction of solid organic materials.

In the late 1980s, the Central Electricity Generation Board (and later, its successor company, Nuclear Electric) began looking for technologies for treatment/disposal of spent ion-exchange resins accumulating at nuclear power stations in the UK. This was both with the aim of volume reduction, and to address concerns about the potential for organic material to enhance radionuclide mobility in a waste repository¹⁴⁰. The preferred method was cementation, but wet oxidation was studied as a contingency, with a preference for a mobile plant where appropriate⁶⁴. A wide range of experiments were undertaken, both at 1 g to 1 kg scale, and 10 kg pilot scale operations. The researchers determined that for cationic resins, FeSO₄ alone was a suitable catalyst, whereas anionic resins demonstrated a strong synergy when FeSO₄ and CuSO₄ catalysts were utilised in combination. Pilot-plant scale studies were undertaken at the Berkley Nuclear Laboratories, using a 0.1 m³ reactor, with combined liquid circulation loop, condenser, gas analysis train and off-gas treatment loop⁶⁴. Batches of up to 10 kg of resin were treated, with achieved destruction rates of 2–2.5 kg h⁻¹ (damp resin) for Lewatit DN resins, although noting some reduction in efficiency if resins contained vanadium from decontamination. Cementation of the oxidation residues was proposed (using a blast furnace slag (BFS)/Portland cement (OPC) blend), with a flowsheet for plant inputs/outputs produced—Table 3, details the mass balance of inputs/outputs for treatment of 1 m³ IER in the proposed plant. Also in the late 1980s, the UK Atomic Energy Authority (UKAEA) and Nuclear Electric began scoping treatment options for sludges arising from the Steam Generating Heavy Water Reactor (SGHWR) at Winfrith¹⁴¹. These sludges arose from plant operations (moderator purification, pond cleanup, and primary circuit decontamination)

Table 3. Input/output for proposed CEGB wet-oxidation plant⁶⁴.

Inputs	Outputs
1 m ³ Lewatit resin	950 kg CO ₂
2 m ³ water	400 kg O ₂
10 kg FeSO ₄	6300 kg steam
5000 kg H ₂ O ₂	60 kg NaSO ₄
	60 kg CaSO ₄
	10 kg Fe ₂ O ₃
	300 kg water
<i>Final product</i>	
730 kg BFS/OPC	0.6 m ³ wasteform

and were stored in tanks on-site. They comprised 65% powdered ion-exchange resins (Powdex, 2:1 cation:anion), 20% hydrated lime (added to reduce supernatant activity, allowing sea discharge of liquors), 5% corrosion product oxides (Fe, Cu, Ni, Mn, V), 3% diatomaceous earth, 2% cellulose and various decontamination liquors (various organic acids, nitric acid and ammonium oxalate)^{142,143}. Wet-oxidation trials of these wastes started with inactive lab-scale testing followed by a 1–10 kg pilot plant, then a 200 kg scale demonstration plant—with the aim of developing a full-scale plant coupled up to a cementation plant¹⁴¹. This was a batch operation process, with no initial acidification or catalyst added (trials were performed with both catalyst and acid, but with little improvement). Carbon removal of ~96% was achieved, with the ability to reach 99% although this required a high volume of peroxide. Hot trials were undertaken using 100 kg of real waste, resulting in a 60% reduction in total solids¹⁴¹. Post-processing analysis showed 100% of the initial α activity was retained within precipitated solids, though β and γ activity were split between solids and supernate¹⁴¹.

Following lab-scale testing, a 1/15th scale demonstration plant was developed, capable of operating under reflux. This was completed in 1989 and designed to operate with batches of 200 kg sludge (with 300 g kg⁻¹ solids content). Building on this experience, a design study for a full-scale plant was

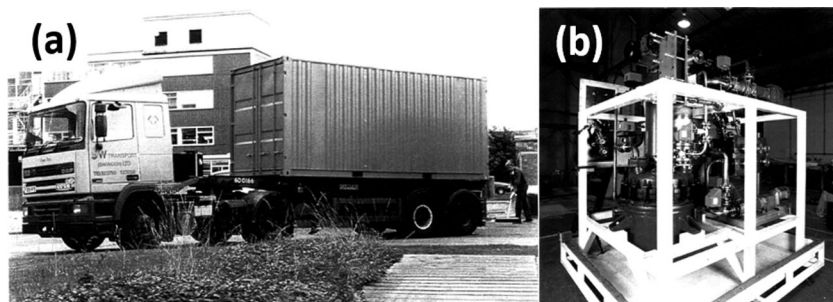


Fig. 5 AEA mobile wet-oxidation rig. Plant within mobile transportation (a), reaction vessel and main plant section (b)¹³. Reproduced with permission from ref. ¹³, copyright (EC, 1996).

commissioned, with the preferred option to retrofit a wet-oxidation system to the head end of a cement encapsulation plant (under construction at the time). Within this plant specification was an overall claimed potential volume reduction of at least 2.5, with reduced organics and potential cost saving—although volume reduction would be limited due to inorganic content within the wastes¹⁴¹.

Ultimately the decision was made not to pursue wet oxidation for SGHWR sludges, opting for decay storage of wastes until 2012, then cementation¹⁴³. The cementation route was, however, cancelled due to changes in waste acceptance criteria at the UK Low Level Waste Repository (too high ⁶³Ni and ¹⁴C levels for disposal). Cementation was later re-adopted, with an on-site cementation plant constructed, cementing the sludge into 500 L drums^{142,144}. These drums are themselves packed into 2/3 height IP-2 ISO containers (which will be grouted prior to disposal)—resulting in a final packaged volume of 1974 m³ (from an original volume of 330 m³ prior to treatment¹⁴⁵) and consigned to the UK Low Level Waste Repository (LLWR, having now decayed enough and diluted by cementation)¹⁴⁴.

Although an alternative route was selected for the SGHWR sludges, research on a wet-oxidation rig was continued by UKAEA's recently formed commercial arm AEA Technology through the 1990s as part of a European Commission R&D programme. This programme of work spanned over 4–5 years, with the aim to review suitable wastes for wet oxidation, scale testing at both inactive and active level, then construction of a mobile wet-oxidation pilot plant capable of processing was at a rate of 50–100 kg d⁻¹^{13,63,136,146–148}. Initial literature studies concluded that wet oxidation of IERs held the most promise, followed by treatment of transuranium contaminated cellulosic wastes, and decontamination liquids/scintillation cocktails not currently compatible with existing disposal routes¹⁴⁶. Small-scale trials were undertaken using Fe²⁺ and mixed Fe/Cu catalysts, with a semi-continuous process chosen for H₂O₂ efficiency¹⁴⁶. By 1992 the design of a mobile wet-oxidation plant was completed, along with further lab trials on suitable wastes—with claimed 'efficient organic removal'. They trialled the decomposition of Lewatit DN ion-exchange resins, and Lewatit DN + inorganic zeolites (both used for ¹³⁷Cs removal in fuel storage ponds in UK)¹⁴⁷.

Construction of a mobile pilot plant was completed in 1993, with first reactions using inactive IX resin as part of commissioning¹⁴⁸. The plant was fully contained in one ISO container, with a jacketed reaction vessel, waste feed hopper, feed/discharge pumps, and coil heat exchanger—shown in Fig. 5. It was designed for up to 50–100 kg d⁻¹ throughout, with a maximum activity of 0.1 TBq as ⁶⁰Co. The container also included a distillate tank, packed tower acid scrubbing column and HEPA filters for gaseous discharges. The main hazard was determined to be dose to workers; however, the system could be remotely controlled to manage dose uptake¹⁴⁸. The wet-oxidation rig utilised sulphuric acid and Ca(OH)₂ solution for pH control, along with Fe²⁺ and

Cu²⁺ catalysts (sometimes equilibrated with wastes for up to 24 h beforehand). The rig was heated to 90 °C, pH adjusted to a set point (and adjusted throughout, mostly with alkali additions otherwise highly acidic conditions prevailed), then peroxide added at a constant rate. Anti-foaming solution was added when required, and post-processing the resultant liquid/sludge was neutralised to pH 7–8 with Ca(OH)₂¹³. A packed tower scrubbing column was required for off-gas treatment, with 10% sulphuric acid utilised to neutralise ammonia/amines from anionic IER degradation. Overall the majority of radioactive species remained in the supernatant / sludge—however, some ⁶⁰Co was noted to carryover to aqueous distillate, especially in frothing samples, along with ~90% of tritium in treated samples. A summary of wet-oxidation trial experimental conditions are noted in Tables 4 and 5.

Further testing, including active tests using ion-exchange resins were conducted using the pilot plant throughout 1994⁶³. Non-active trials included mixed ion-exchange resins from Magnox plant condensate polishing/steam boiler cleanup, steam generator decontamination liquor simulant, and simulated SGHWR sludge. Treatment of the mixed IERs claimed a 96–99% carbon removal, with a 86–92% volume reduction (dry product), with residues consisting of a mix of calcium/metal sulfates, calcium hydroxide and organic residue in a weakly ammoniated aqueous phase. Active trials consisted of 250 L of PWR mixed bed resins from cooling pond water cleaning (IRN 77 and IRN 78), spent IER from decontamination of a small PWR reactor containing organic chelating agents (likely submarine origins), and active SGHWR sludge^{13,63}. Hot tests were particularly successful, with an average ~95% original carbon removal, with 63–69% peroxide utilisation efficiency (e.g. ~4 t 50% H₂O₂ m⁻³ flooded PWR resin), although problems were encountered monitoring pH in situ (high dissolved organics, suspended solids, high temperature).

This project resulted in a final technical report in 1996 entitled 'Wet oxidation of organic radioactive waste', detailing the 5 year programme, technical data on experimental runs, and mass balances for wastes¹³. The report also summarises the previous lab-scale experiments, with the most successful experiments arising from this programme detailed in Table 4. The final conclusions of this report note the success of wet oxidation for several organic radioactive wastes, with an achievable throughput of 30–50 L organic waste in an 8 h day, using a semi-continuous process. No detectable emissions above background were detected from gaseous emissions, with secondary liquid wastes suitable for discharge to a standard radioactive effluent treatment system. Cementation of solid wastes claimed to be successful, with a full-scale oxidation plant estimated to reduce the volume of conditioned IER resins by 65% compared to direct cementation, with cost savings due to reduced space required in a deep geological disposal facility. The implementation of this mobile rig was detailed in the final report, with extensive information about mass balance for proposed waste treatment, noted in Table 6. The

Table 4. Most successful (highest % organic carbon reduction) lab-scale runs from first AEA wet-oxidation programme¹³.

Waste	Active	Oxidant	Catalyst	pH	Organic carbon reduction
Lewatit DN (cation IER)	N	H ₂ O ₂ 50% 5.1 t m ⁻³	Fe ²⁺ 4.7 kg m ⁻³	2.0	99%
Amberlite IRN150L (mixed IER)	N	H ₂ O ₂ 50% 6.6 t m ⁻³	Fe ²⁺ 4.0 kg m ⁻³ Cu ²⁺ 1.0 kg m ⁻³	4.0	96%
Powdex (mixed IER)	N	H ₂ O ₂ 50% 5.64 t m ⁻³	Fe ²⁺ 2.4 kg m ⁻³ Cu ²⁺ 0.6 kg m ⁻³	4.0	95%
Lewatit/AW500 (3:1 organic: inorganic)	N	H ₂ O ₂ 50% 4.8 t m ⁻³	Fe ²⁺ 1.0 kg m ⁻³ Cu ²⁺ 1.0 kg m ⁻³	3.5	88%
Lewatit/Descalo Y (3:1 organic: inorganic)	N	H ₂ O ₂ 50% 4.8 t m ⁻³	Fe ²⁺ 1.0 kg m ⁻³ Cu ²⁺ 1.0 kg m ⁻³	3.5	86%
SGHWR sludge (semi-cont reaction)	N	H ₂ O ₂ 50% 2.0 t m ⁻³	None added, present in waste	3.5	93–96%
Lewatit DN (semi-cont reaction)	N	H ₂ O ₂ 50% 3.6 t m ⁻³	Fe ²⁺ 1.2 kg m ⁻³	2.0	95%
Trawsfynydd resin (Lewatit/AW500)	Y	H ₂ O ₂ 50% 5.0 t m ⁻³	Fe ²⁺ 1.0 kg m ⁻³ Cu ²⁺ 1.0 kg m ⁻³	3.5	97%
Cellulose waste (paper, tissue, cloth)	N	H ₂ O ₂ 50% 1.4 t m ⁻³	Fe ²⁺ 2.5 kg m ⁻³ Cu ²⁺ 2.5 kg m ⁻³	3.0	95%
1% citric acid	N	H ₂ O ₂ 50% 0.044 t m ⁻³	Fe ²⁺ 0.2 kg m ⁻³ Cu ²⁺ 0.2 kg m ⁻³	2–4	99%
1% formic acid	N	H ₂ O ₂ 50% 0.018 t m ⁻³	Fe ²⁺ 0.1 kg m ⁻³	2–3	99%
1% EDTA	N	H ₂ O ₂ 50% 0.05 t m ⁻³	Fe ²⁺ 0.2 kg m ⁻³ Cu ²⁺ 0.2 kg m ⁻³	3–4	99%
Scintillant residue (1% organics)	N	H ₂ O ₂ 50% 0.084 t m ⁻³	Fe ²⁺ 0.2 kg m ⁻³ Cu ²⁺ 0.2 kg m ⁻³	2–3	94%

treatment of ~1100 kg waste would require 4000–5000 kg of 50% H₂O₂, resulting in 5000–7000 kg of aqueous distillate, along with ~600–1100 kg of treated product, itself predominantly water, sulfates, calcium and residual carbon amongst other minor components.

Testing of the AEA wet-oxidation rig continued with another 4 year EC project, looking at application to a wider range of organic wastes in Europe, including ion-exchange resins from the German Krümmel and UK Oldbury NPPs, and liquid wastes at the Belgian BelgoProcess site^{149,150}. Various modifications and upgrades to the rig (now called ModulOx) were undertaken to improve throughput and control systems (waste feed improvements, pH measurement, improved logging system, etc.). Overall the system chemistry remained largely the same, utilising 50% H₂O₂ with sulphuric acid and Ca(OH)₂ or NaOH for pH control. Fe²⁺ and Cu²⁺ were utilised as catalysts, with cementation of sludge/residue formed from IER destruction¹⁵⁰.

The system successfully completed a trial run of dried mixed bed resins shipped from the Krümmel NPP to the UK, with waste sludge encapsulated within a BFS:OPC cement blend to German standards allowing disposal at Morsleben, with a claimed 80% waste volume reduction compared to direct cementation of untreated resins. The rig was also transported to Oldbury NPP in the UK for similar treatment of spent lithiated IERs; however, this time occurring on-site as a demonstration of the mobile aspect of the rig. Treatment was successful, with resultant waste encapsulated in a PFA:OPC (Pulverised Fuel Ash) cement blend, with a claimed 49% final product volume reduction. Further demonstration of the mobile rig occurred at the BelgoProcess site in Belgium, where ~2900 L aqueous liquid wastes containing up to 68,000 mg L⁻¹ COD (Chemical Oxygen Demand) were treated to a resultant COD of 70–114 mg L⁻¹, with resultant effluents directed into the existing site effluent treatment system¹⁵⁰. Overall the trial treatment of various wastes was deemed successful at the various sites, with rig portability firmly established, though with some

issues relating to extra temporary shielding requirements, and outdoor operation/situation of the rig. The development of the modular rig did not appear to continue much further in the UK after this project finished, despite achieving the goals of successful waste treatment.

The ModulOx system was, however, tentatively planned for usage in treatment of specific UK nuclear submarine ion-exchange resins. These MODIX resins (Multi-stage Oxide Decontamination with Ion eXchange) had been utilised as part of reactor decontamination, principally to remove ⁶⁰Co^{151,152}. The ¹⁴C content of these spent resins, and presence of chelating agents resulted in these being excluded from the UK Low Level Waste Repository (LLWR), and requiring treatment. The ModulOx pilot-plant at Winfrith was scoped for potential usage, though over the timeframes involved the Winfrith site entered widescale decommissioning prior to advancement of this plan^{152,153}. An additional opportunity arose when a ModulOx rig was shipped to the USA for treatment of ion-exchange resins at Oak Ridge National Lab (ORNL), then to Idaho National Laboratory (INL) for tank waste remediation¹⁵⁴. Ultimately this rig was not utilised for planned waste treatment at either location due to project amendments or usage of alternative technologies.

In 2014, the UK Nuclear Decommissioning Authority reviewed experience of mobile ILW plants in Britain, coming to a pessimistic conclusion on mobile wet-oxidation plants¹⁴. Originally designed to avoid large fixed installations and to allow acceleration of hazard reduction programmes, mobile rigs suffered from problems due to their compact size. This resulted in low throughput, hazardous maintenance due to tightly packed equipment, higher operator dosage (or requirement for shielding to be constructed), staffing issues and potential lack of flexibility with various wastestreams. Delays on one site would impact another, and discharge permits might require alteration due to a change of process on-site (i.e. amendment to gaseous discharge licence). The initial wet-oxidation rig, though designed for a 100 L IER per day,

Table 5. Wet-oxidation trials at plant operation level^{13,63}.

Waste	Active	Oxidant	Catalyst	pH	Organic carbon reduction	Duration
Spent PWR resins (250 L)	Y	50% H ₂ O ₂ 1 t	Unspecified	–	96%	2× semi-cont runs over 48 h runtime
Small PWR reactor decontamination resins (360 L)	Y	50% H ₂ O ₂ 1.6 t	Unspecified	–	95%	3× semi-cont runs over 58 h
SGHWR sludge (177 kg inactive, 1 kg active)	Y	50% H ₂ O ₂ 480 kg	Unspecified	–	94%	18 h
Lewatit DN KR cation resin (113 L)	N	50% H ₂ O ₂ 591 kg	Unspecified	–	94%	45 h
Steam generator decontamination liquor simulant (CuSO ₄ , FeSO ₄ , EDTA, ammonia, water) (116 L)	N	H ₂ O ₂ 56 kg (unspecified %) (0.48 t m ⁻³)	CuSO ₄ and FeSO ₄ in liquor	–	99.1%	3 h
Mixed bed IER (IRA 900 and Ambersep IR252) (520 L total over 4 runs)	N	50% H ₂ O ₂ 2.9 t m ⁻³ at 0.5 kg min ⁻¹	CuSO ₄ ·5H ₂ O and FeSO ₄ ·7H ₂ O	3.5	~97%	Semi-cont runs, average 13 h reaction time over multiple days excluding heating/cooling
Run 1 (103 L)	N	50% H ₂ O ₂ (2.7 t m ⁻³)	FeSO ₄ ·7H ₂ O (740 g) CuSO ₄ ·5H ₂ O (150 g)	3.5	99.2%	10 h
Run 2 (125 L)	N	50% H ₂ O ₂ (2.9 t m ⁻³)			98%	12 h
Run 3 (125 L)	N	50% H ₂ O ₂ (2.7 t m ⁻³)			97%	11.5 h
Run 4 (165 L)	N	50% H ₂ O ₂ (3.2 t m ⁻³)			96%	18 h

Table 6. Mass balance for treatment of 1 m³ various wastes in a mobile wet-oxidation plant, data taken from¹³.

Inputs (kg)						
	Waste	Water	H ₂ O ₂ (50%)	Acid/alkali	Additives ^a	Scrubber liquor
PWR IX resin	1100	700	4000	1302	44	200
Spent IX resin (mixed decon)	1100	1551	4600	1451	44.2	200
SGHWR sludge	1200	559	3171	1938	35.53	71
Lewatit DN KR cation resin (inactive only)	1150	1820	5260	1637	141.5	0
Outputs (kg)						
	Treated product total	Largest components of treated product		Aqueous distillate	Off gas	Scrubber liquor
PWR IX resin	601.22	391 water 122 sulfate	54 calcium 11 carbon	5538	1026	208
Spent IX resin (mixed decon)	581.77	378 water 102 sulfate	66 calcium 11 carbon	7007	1171	208
SGHWR sludge	848.10	551 water 159 sulfate	98 calcium 25 other ions	5172	814	74
Lewatit DN KR cation resin (inactive only)	1116.00	725 water 259 sulfate	64 calcium 44 sodium	7624	1396	0

^aAdditives largely comprising water, anti-foaming agents and catalysts (Fe, Cu sulfates).

only treated 360 L over its lifetime (due to never seeing full operation), and the rig still required an encapsulation plant to solidify the residues. On a more positive note, it was concluded that trials on fixed wet-oxidation plants appear to suffer from fewer concerns than fully modular systems¹⁴.

Japan

Wet oxidation in Japan was initiated at the Japan Atomic Energy Research Institute (JAERI) in the early 1980s, with research quickly

moving into an industrial setting, and further advancements largely led by the Japan Gasoline Corporation (JGC), along with some research by other industrial sector companies. This early research was detailed by Kubota at JAERI, resulting in the publication of two Japanese patents in 1982. The first details destruction of a cationic resin with hydrogen peroxide and a chromium or iron nitrate catalyst¹⁵⁵, the second details destruction of an anionic resin with peroxide and chromate/bichromate ions¹⁵⁶. Alongside this was a 1983 paper detailing investigation into cation exchange resin degradation with H₂O₂ and Fe³⁺¹¹. In

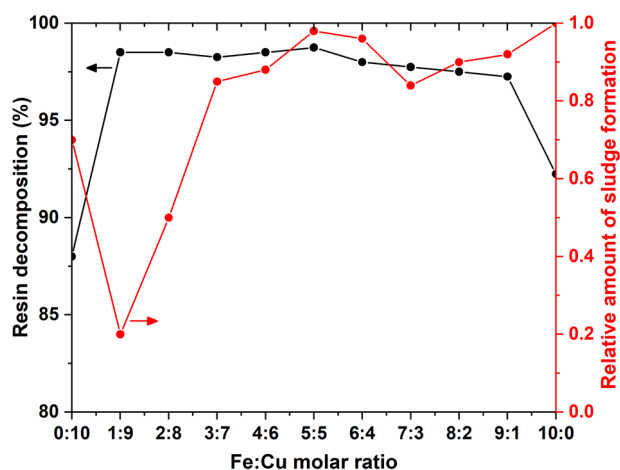


Fig. 6 Effect of Cu:Fe catalyst ratios on decomposition and sludge formation. Data adapted from ref. ⁵⁹ for clarity.

the same year Nippon Atomic Industrial Group and Tokyo Shibaura Electric Co briefly stepped into this research, being granted a patent detailing IER decomposition with H_2O_2 and a ferric sulfate solution, although with no noticeable innovations over the JAER patents¹⁵⁷. This was followed by two further patents in 1984 detailing ion-exchange treatment with ferric sulfate and peroxide¹⁵⁸, and a patent utilising Cu ions as catalysts for anion-resin degradation with an electrochemical method of Cu recovery¹⁵⁹.

The Japan Gasoline Co. continued this line of research, publishing a wealth of patents and conference papers detailing their research from 1983 onwards. These heavily focus on destruction of ion-exchange resins, usually for volume reduction purposes. Their rationale stems from the claim that many alternative treatment options for IERs either require very strong acids and result in highly corrosive liquids/gases, or risk radionuclide migration into gases from high-temperature processes, requiring complicated off-gas systems. Many of the patents detail conventional Fenton-like systems, utilising a transition metal catalyst (typically ferric sulfate) and hydrogen peroxide at, or near-boiling temperature. Ion-exchange resins, chelate resins and various organic filter aids are decomposed. Several patents also detail equipment setup for oxidation, then drying and solidification systems coupled to this.

A notable finding by JGC (and echoed elsewhere) is the relative difficulty of anion-resin degradation compared to cation resins. Their method claimed to improve degradation by addition of even a small amount of Co or Mn, or by co-processing anion and cation resins together. It was claimed that co-processing even 1% cation resins alongside anion resins results in a marked increase in degradation^{160,161}. Efficiency improvements were sought, with several patents describing usage of refluxing vessels rather than condensation and collection of distillate^{162,163}, along with various processes for continuous feeding of waste and/or peroxide into a reactor vessel¹⁶⁴, one of which specified an average residency of 2–6 h¹⁶¹. JGC further outlined a full system for decomposition, then drying and packing of wastes for solidification¹⁶⁵.

Aside from treatment of solid organic material, JGC also adapted their Fenton system for the treatment of various radioactive waste liquors (detergents and/or liquid organics)¹⁶⁶, and for treatment of decontamination agents, including organic acids (EDTA, citric acid, etc.), the latter utilising Cu and Fe catalysts¹⁶⁷. This treatment of decontamination agents appears to have been taken further, up to pilot-plant scale treating 150 L of solution. The system utilised combined Fe and Cu catalysts to almost completely decompose organic acids, with a claimed efficiency of 5–10 kg of 35% H_2O_2 kg^{-1} of decomposed EDTA¹⁶⁸. A

large reactor (effective volume of 111.4 m^3) is mentioned two years later, for treatment of liquid effluents, coupled to a UV system for complete decomposition. This second system also utilised Fe and Cu catalysts, but with continuous feeding of waste, 50% H_2O_2 , anti-foaming agent addition and pH control to 3–4 with H_2SO_4 ¹¹⁴. It is unclear whether these processes were developed further than pilot scale, with little publicly available information since 1990.

Later, the JGC wet-oxidation process was re-assessed for application in volume reduction of spent ion-exchange resins at the Tsuruga nuclear power plant in Japan. This is the oldest commercial reactor in Japan, with unit 1 currently undergoing decommissioning. A suitable solution was required for stored IERs and filter sludge on-site (>500 m^3 combined volume in 2003)¹²⁷. Though the IERs were wholly organic, the filter sludge was a combination of cellulose, diatomaceous earth, metal oxides and IERs. It was concluded that a 'conventional' H_2O_2 + ferric/ferrous ion Fenton system would be suitable for waste volume reduction¹²⁷. This option does not appear to have gained further traction, however, the option of Tsuruga NPP IER treatment using wet oxidation was revived again in 2011, with JGC and JAPC undertaking further research. Pilot scale tests were claimed to be successful, with wastes compatible with super-cement solidification (an alkali activated cement developed in Japan)^{128,169}. Since this time Tsugura unit 1 is undergoing decommissioning, but no public information regarding any implementation of wet oxidation is available.

Although the bulk of open research has been undertaken by JGC, several other groups in Japan have researched or been granted patents on wet oxidation of nuclear wastes. As noted earlier, Nippon Atomic Industrial Group and Toshiba have been granted several wet-oxidation patents^{157–159}, although one of the more notable achievements was by Fuji Electric. In 1988 they were granted an extensively researched patent for Fe/Cu catalysed oxidation of IERs¹⁷⁰ (1989 for US patent⁵⁹). Innovations in this patent include crushing of IER prior to oxidation, resulting in reduced H_2O_2 required and lower foaming. A net weight of H_2O_2 to dry IER no higher than 17 (i.e. 17/1) was recommended, preferably between 10 and 4, or with citric acid adsorbed onto IERs prior to decomposition. It was noted that Fe and Cu catalysts combined can work at neutral pH, but lower pH is needed to avoid the build-up of sludge (so recommended to keep pH 2–3). Mixed catalysts were found to work better than Fe or Cu alone, although the molar fractions were not important. A 9:1 Cu:Fe catalyst was found to work just as well, but with less sludge formation (which was directly proportional to Fe content in catalyst—noted in Fig. 6). The composition of anion resins was also found to be crucially important, with anion IER decomposition decrease in efficiency from citric acid > SO_4 > OH > Cl types. From this they claim that citric acid sorbed onto resins prior to treatment resulted in high degradation efficiency⁵⁹, with this potentially being due to reduced sludge formation.

Despite a wealth of patent literature and widescale research, no large-scale deployment of Fenton-like wet oxidation in Japan on a commercial scale is evident from open literature.

USA

Fenton-like wet-oxidation processes have not found sure footing within the USA. Several pilot scale trials have been undertaken with wastes, with wet oxidation scoped for technology development—but has not progressed beyond this. The US Atomic Energy Commission obtained a patent for Fenton oxidation of spent ion-exchange resins in 1972¹⁷¹. This was, however, for removal and retrieval of nuclear material from IERs (Pu, U, Th, Ac) rather than with a focus on waste reduction. The method envisages dissolving resins in nitric acid and hydrogen peroxide, catalysed by potassium ferrocyanide, with several examples showing Pu

removal from resin. Overall this particular process neither appear to have been further built upon, nor enjoyed industrial-scale usage.

Interest was later gathered for the demonstration of wet-oxidation technology in the 1990s. The Mixed Waste Management Facility (MWMF) was planned to be built at Lawrence Livermore National Laboratory (LLNL), and envisaged as a national test bed for four different demonstration technologies, all aiming to treat low-level waste arising from sites in the USA^{172,173}. This included molten salt oxidation (MSO), mediated electrochemical oxidation (MEO), ultraviolet photolysis (UVP) and wet oxidation (WOX). The UVP system was to be utilised on effluents from the WOX system, as an organic polishing system to further reduce organic material down to regulatory limits. Unfortunately, this facility does not appear to have been constructed in its envisaged form, with budget amendments focussing efforts on molten salt oxidation only, and WOX work closed out per Department of Energy guidance by 1997 onwards¹⁷⁴.

Interest was renewed in utilisation of Fenton chemistry in the early 2000s, with laboratory scale testing undertaken for destruction of wastes at Oak Ridge¹⁷⁵. A mix of transuranic sludges and organic IERs were located in underground storage tanks (T1 and T2 tanks) in the Melton Valley watershed. It was determined that not enough plutonium could be leached from the wastes using acid or chelates to render the waste non-transuranic in classification, therefore destruction of the resins remained the only option, enabling the wastes to then be treating using on-site facilities. Lab-scale testing, then active pilot scale testing was undertaken using real waste. AEA Technology was chosen to build and operate a full-scale system to treat both tanks, along with the nearby High Flux Isotope Reactor (HFIR) tank waste. Treatment of tanks was planned for 2004, with a large modular skid mounted oxidation rig constructed and delivered to site^{154,175} (photograph of reactor module in Fig. 7). Further characterisation, however, determined that wet oxidation was not required to meet waste acceptance criteria, with wastes suitable for treatment at the on-site LLW evaporator, with tanks subsequently grouted¹⁷⁶.

This rig, based on AEA's ModulOx technology, quickly found another use, and was shipped to Idaho National Laboratory (INL) for usage in treating V-Tank waste¹⁵⁴. The modular system included a 2.27 m³ (600 gallon) internal volume reactor (operating in reflux mode) with scrubbing system, off-gas skid (with HEPA and GAC filter), control trains, along with a steam generator and chilling system. The rig was to act as a backup secondary treatment of V-tank wastes if air/ozone sparging of wastes was not fully successful in reducing VOC content enough for disposal. Despite intermittent operation of sparge treatment, the



Fig. 7 Photograph of reactor module at Oak Ridge¹⁵⁴. (Copyright © by WM Symposia. All Right Reserved. Reprinted).

programme at INL had treated over 61,000 L of waste by 2007, with post-sparged wastes mixed with a water absorbent material and disposed of at the Idaho CERCLA Disposal Facility (ICDF), ultimately resulting in no need for usage of the AEA rig¹⁷⁷.

The only other publicly cited use of Fenton oxidation for nuclear waste or site cleanup in the USA was a brief demonstration of subsurface decontamination at the Savannah River Site (SRS) in 1997. Organic destruction for soil remediation using peroxide and iron catalysts is a proven technology with commercial vendors, having been applied to a range of challenging organics^{178–180}. At SRS, dense non-aqueous phase liquids (DNAPL) were targeted for in situ destruction using a combination of H₂O₂ and FeSO₄ injected underground. Destructive efficiency of 94% for DNAPLs was achieved, but with a lasting impact on soil pH due to acidic media utilised^{180,181}.

Overall Fenton oxidation processes have never fully been utilised for large-scale waste processing in the USA, although the AEA rig nearly found usage for dealing with several niche wastestreams. A particularly complicating factor in assessing Fenton and Fenton-like oxidation processes in the USA is the usage of the term 'wet oxidation' for both a Fenton-like process, and for higher pressure/temperature catalytic wet oxidation using air/oxygen. There is also some confusion within literature between a Fenton-like process and catalysed acidic chemical oxidation (also known as 'direct chemical oxidation'), such as the Delphi Detox process which gained some traction for organic waste disposal in the USA^{182–184}.

Canada

Although never operating a commercial Fenton-like wet-oxidation process, Canada requires recognition for operating a 'WETOX' process, which has sometimes been confused for a Fenton-like system. In the 1980s the Ontario Research Foundation undertook research and early commercialisation of a higher pressure and temperature wet air oxidation system (350–400 °C, 40 bar) for treatment of aqueous wastes^{185,186}. This was continued by Ontario Hydro, whom in the mid 1990s operated a plant at the Bruce NPP for processing wastes containing high concentrations of EDTA and metal ions (principally iron and copper) from cleaning steam generators¹⁸⁷. This plant utilised high pressure steam at 250 °C and pressures of 5 MPa, with the plant treating >5 million litres before shutdown and decommissioning¹⁸⁸.

ECONOMICS

The principal economic driver for Fenton oxidation of radioactive organic wastes is the potential for the volume reduction of wastes. If wastes are to be consigned to engineered disposal facilities (e.g. shallow burial for lower activity wastes, or deep geological disposal for higher activity), these may entail significant costs per cubic meter of waste. Additionally, if these facilities are not yet operational or accepting wastes, ongoing costs from interim storage in suitable facilities may be incurred.

Cost estimates for treatment of nuclear wastes have varied greatly, and few reports have assigned full costings to waste treatment—instead focussing on estimates of volume reduction. A 1987 Swedish study claimed a volume reduction factor of 15 was achievable⁷⁵, while a 1989 initial study in the UK estimated volume reductions of a factor of 5 were achievable, with subsequent cementation of the wastes resulting in a net saving on storage and disposal costs, although no final figures were reported⁶⁴. A UK pilot-plant wet-oxidation rig operating in the 1990's claimed a 66% volume reduction for organic ion-exchange resins with cementation of partially dried sludges, versus direct cementation. Drying then compaction of the wastes without cementation was claimed to result in a 95% volume reduction¹³. The authors calculated upfront capital costs, staffing,

maintenance, discharge licences, chemicals, etc.—noting this was in addition to cementation post-treatment. Costings for a 1/10 scale pilot plant (in 1995 GBP£) resulting in £42,000 m⁻³ of ion-exchange resin treated, with a full sized mobile plant costing £11,000 m⁻³. Overall this resulting in an estimated 51% saving compared to direct cementation of the resins, principally coming from the reduced final volume of the wasteforms.

No more recent open literature assessments of waste treatment economics using Fenton oxidation are available, and economics are highly likely to vary from country to country, and waste to waste. Equally, other regulatory concerns will factor into waste treatment options other than straight economics. There may exist limits on the type and quantity of organic material permitted within an engineered repository, particularly for chelating organics. These are of concern due to the risk of enhancing radionuclide mobility and may, for example, push regulators towards recommending various thermal treatment technologies for waste treatment.

CONCLUSIONS

Fenton and Fenton-like wet oxidation of radioactive wastes has been championed for destruction of organic materials for around 40 years, due to the attractive option to significantly reduce solid waste volumes and potentially re-categorise wastes for acceptance into national repositories. The presence of organics, especially organic complexants, are sometimes restricted due to concerns over flammability, degradation of organics over time and potential increased mobility of radionuclides.

Extensive trials on the implementation of wet oxidation have been undertaken in Italy, Sweden, Japan, USA and the UK. Laboratory scale research, pilot plants and multinational trials have determined that volume reduction and adequate destruction of certain materials are achievable. Wastes targeted in these trials include ion-exchange resins, waste reprocessing solvents, sludges and decontamination liquors. Typically wastes have been treated in batch, or semi-batch processes, with remnant solids sent for cementation and liquid effluents disposed via other routes.

Many of these national trials have focussed on specific challenging wastes (e.g. EUREX solvents in Italy). The most extensive testing at varying levels has been in the UK, with several scale pilot plants and mobile plants, which have treated varying ion-exchange resin, sludges, cellulosic waste and liquid organics, including active trials utilising real wastes. On the back of these research programmes around the world, several full-scale wet-oxidation plants were planned for construction, usually utilising conventional Fe–H₂O₂ Fenton chemistry. None of the proposed facilities were ever constructed beyond scaled pilot plants, with more conventional treatment facilities utilised for waste disposal (e.g. incineration or cementation).

In recent years, research has narrowed to focussing specifically on destruction of organic ion-exchange resins, of which notable quantities exist in varying forms across most countries with nuclear power programmes. Different catalysts have proven more successful for decomposing different types of resins. Fe catalysts are favoured for decomposition of strong cation resins, with Cu catalysts favoured for strong anionic (also alongside additions of organic acids) and mixed Fe–Cu catalysts for mixed resins. Only homogeneous catalysts have been trialled, due to the requirement for Fenton reactions to occur at the resin–liquid interface to initiate degradation—utilising the ion-exchange capability of these resins to draw catalysts to the resin surface.

Opportunities and challenges remain with this technology to become a viable industrial treatment process. Although the volume of solid wastes is reduced, Fenton reactions require large volumes of H₂O₂ to degrade the solid resins, resulting in an equally large volume of secondary liquid wastes generated. These liquid wastes have often been overlooked in plans for large-scale

pilot plants, but strict environmental discharge limits for radioactive material will likely necessitate further processing of these wastes either in an enhanced Fenton process, or in additional treatment facilities. Further processing is also required for solids generated, with larger plants typically envisaged to be operated at the head-end of a cementation facility. Due to these additional wastes, longer-term understanding of any final waste-wasteform interactions is required (e.g. between precipitated sulfates and cement), or research into alternative wasteforms (i.e. glass or ceramic materials) for wastes generated. An original hope for wet-oxidation facilities was for smaller, mobile plants which could treat varied wastes across different sites, however, challenges in operating and licencing modular wet-oxidation systems are likely to limit future usage outside of larger fixed plants.

On a more positive perspective, the ability of Fenton wet oxidation to degrade material at lower temperatures is of particular interest for wastes containing volatile radioisotopes, for which high-temperature processes may require extensive off-gas systems. Opportunities exist for optimising degradation reactions with varied catalysts (including metal ions not favoured during typical wastewater treatment, such as copper and chromium), optimising the quantity of H₂O₂ utilised to reduce secondary wastes, co-treatment with other organic materials or integration into an alternative waste immobilisation process (e.g. head-end of a hot isostatic pressing system).

Due to the continued presence and generation of organic radioactive wastes, and a drive towards safe, final disposition of nuclear wastes, Fenton and Fenton-like wet-oxidation research will likely continue to offer solutions and opportunities for nuclear waste management. The potential for lower temperature processing, with significant reduction in resultant solid wastes could provide another technology in the toolbox of treatment options.

DATA AVAILABILITY

No datasets were generated or analysed during this study.

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AUTHOR CONTRIBUTIONS

S.W.—manuscript preparation, formal analysis, reviewing, editing. W.U.—reviewing, editing. C.C.—reviewing, editing. N.H.—supervision, reviewing, editing.

COMPETING INTERESTS

The authors declare no competing interests.

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