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A new coupled non-thermal plasma and sorption method for treatment of liquid radioactive wastes: Design and on-site application to Chornobyl NPP-derived wastes

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ABSTRACT

Higher activity liquid wastes pose a significant management challenge at nuclear sites, and there is a strong drive to develop cost-effective (and more sustainable) waste treatment solutions that can remove radioactive and other contaminants from these liquid radioactive wastes (LRW) prior to their discharge or final storage/disposal. Here, results are presented from an on-site trial of a coupled non-thermal plasma / sorption-based LRW treatment system at the "Dibrova" Object in the Chornobyl Exclusion Zone. Over 2m^3 of Cs-137 and Sr-90 contaminated LRW from settling tanks used for the holding of tailings and drain water from Chornobyl Building № 5 and deactivation solutions (used in the liquidation efforts following the 1986 Chornobyl disaster) were treated. The coupled treatment process removed greater than 90 % of Cs-137 and Sr-90 from the most contaminated liquids (containing 75 Bq/kg (Cs-137) and 195 Bq/kg (Sr-90)), generating a low mass ($<100g$) iron-rich solid residue suitable for onward storage/disposal. Treatment efficiencies for other waste components (e.g. nitrites, phosphates and COD) were equivalent to or exceeded those previously reported for treatment of environmental liquid wastes by similar Advanced Oxidation Processes. The power requirements of the system (due to the pulsed nature of the plasma generated) were relatively low, at 10 kWh, for a LRW treatment rate of 15 - 20 L/h. The system can be operated remotely in autonomous mode, and its modular, easily transportable nature means that the process can be readily adapted for various on-site treatment scenarios.

1. Introduction

Higher activity liquid active wastes and liquors (liquid radioactive wastes or LRW) pose a significant management and disposal challenge at nuclear sites, and there is a strong drive to develop cost-effective (and more sustainable) waste management and treatment solutions that can remove, stabilise or concentrate radioactive and other contaminants from these wastes prior to their discharge or final storage/disposal. Particular difficulties arise around mixed organic-radionuclide wastes, or where radionuclides are complexed with bulk organic ligands or complexants such as ethylenediaminetetraacetic acid (EDTA), which limit the application of conventional liquid waste treatment technologies such as ion exchange, sorption, and precipitation (which generally target ionic or non-complexed radionuclides), and may compromise waste storage or stabilisation safety cases (Cleveland and Rees, 1981; Keith-Roach et al., 2014; Walling et al., 2021; Goo et al., 2024). A prominent example of this is given by the underground storage tanks at the U.S. Department of Energy Hanford site, which contain various organic materials introduced during the production and processing of plutonium, including EDTA, tributyl phosphate, hexone, paraffin hydrocarbons, and other minor organic (and inorganic) components, that may enhance radionuclide migration off-site (Hakem et al., 2001). Further issues may arise from open or unprotected storage of wastes, where algal or microbial growth may generate additional waste condensates or organic sludges which require careful management and disposal (e.g. Foster et al., 2023), or where radionuclide complexation

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with naturally occurring organic molecules such as humic and fulvic acids and their derivatives may occur (e.g. Glaus et al., 2000).

A number of thermal, biological and physico-chemical treatment methods are available for organic-rich or complexed radioactive wastes, including pyrolysis or incineration, bioremediation / biodegradation, and chemical- or photo- oxidation. Of these, pyrolysis / incineration is problematic for larger volumes of liquid waste, and bioremediation or biodegradation may be too slow (and not commercially applicable) for more recalcitrant complexes (e.g. Tucker et al., 1999) or more concentrated radioactive solutions. A number of advanced oxidation processes (AOPs) however have been shown to be capable of effectively degrading radionuclide-organic (including radionuclide-EDTA) complexes under a range of conditions (e.g. Lee et al., 2022), and have been demonstrated at relatively high technology readiness level (TRL) (Walling et al., 2021), allowing liquid waste treatment then subsequent precipitation, ion-exchange or other separation of radioactive species. The more common AOPs such as Fenton's reagent or peroxymonosulfate (PMS)-based processes (and derivates such as electro-Fenton processes) require acidic wastes for optimal performance, which is an issue where LRW have neutral or alkaline pH (e.g. in the case of evaporator concentrates or similar processing or decommissioning residues) and may generate significant treatment residues and sludges (e.g. Zhao et al., 2023). A sub-set of AOPs, non-thermal (or cold) plasma treatment, is however potentially effective for alkaline (or neutral pH) wastes treatment, with the additional advantages of lower chemical input requirements and potentially lower treatment residue generation.

The non-thermal plasma (NTP) process uses plasmas generated at temperatures of around 60 °C and at atmospheric pressure (Kaur et al., 2024): this is possible as the ions within the plasma remain at lower temperatures, while the electrons in the plasma are at higher temperature. In its most fundamental form, an arc discharge is used to generate NTP in a fluid – in the system tested and described here, a microbubble plasma is generated by pulsed electric discharge at the air/water interface in the treated liquid wastes, with coupled hydrodynamic cavitation. This forms highly reactive oxidising species (ROS) such as hydrogen peroxide (H_2O_2), atomic oxygen ($O^{\bullet}$), hydroxyl radical ($HO^{\bullet}$), hydroperoxyl radical ($HO_2^{\bullet}$), and ozone (O_3), which diffuse through the air-liquid interface (both from the overlying air body and via microbubbles generated in the liquid) and interact with the contaminants. The microbubbles increase the surface area to volume ratio of the plasma, and the subsequent collapse of microbubbles due to hydrodynamic cavitation releases reactive species generated by the plasma, increasing the rate of target pollutant degradation (Shahsavari and Zhang, 2023). In addition, when nonequilibrium high voltage nanosecond pulsed plasma discharges are used, as here, these generate UV light emission and create shock waves, increasing the contaminant treatment potential and efficiency. Small scale batch reactor systems using this process have been tested in the University of Southampton laboratories and demonstrate Co-EDTA destruction in high pH, saline wastes at low power consumption (0.04 kWh) (Fig. 1), and published experimental studies have shown the effectiveness of non-thermal plasma for dyes and pharmaceutical residues treatment in wastewater (Mumtaz et al., 2023; Shahsavari and Zhang, 2023), and for gas capture and conversion (Li et al., 2021). Key challenges remain however around (i) system energy demand / operating cost (e.g. Naicker et al., 2023), (ii) scaling treatment volumes cost-effectively (i.e. by ensuring plasma distribution throughout the treated waste volume, and using pulsed, lower energy systems), (iii) minimising treatment residue volumes, and (iv) (for nuclear waste treatment applications) demonstrating at scale on real liquid radioactive wastes, with non-thermal plasma systems largely applied to date in medicine and food industries rather than for liquid wastes and wastewater treatment (Mumtaz et al., 2023).

The overall aim of the work presented here was to develop a flexible modular system for treatment of liquid radioactive wastes (LRW) using non-thermal nonstationary plasma processes combined with sorption, and test this system (on-site, at pilot-scale) on legacy medium-active liquid wastes from the Chornobyl nuclear power plant (NPP). The following areas are presented and discussed below: (a) the design of a pilot-scale non-thermal plasma-based system for LRW treatment; (b) testing of the efficiency of the system for on-site LRW treatment in the Chornobyl Exclusion Zone (ChEZ); and (c) optimisation of the treatment parameters to enable post-treatment liquids to meet the requirements for site wastewater discharge or re-use.

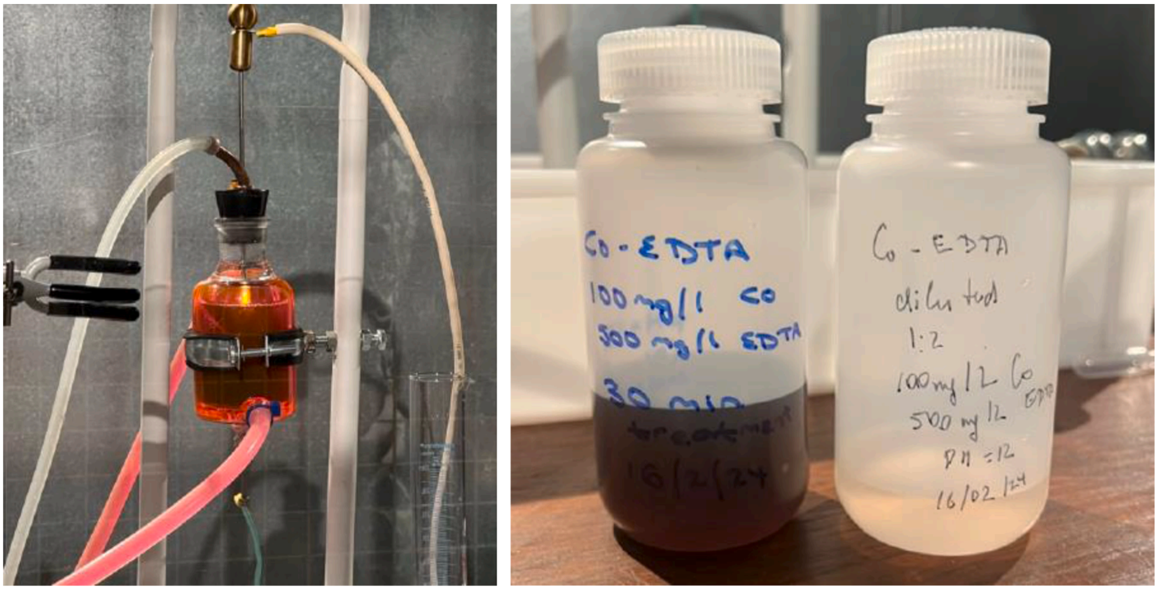

Fig. 1. Static non-thermal plasma batch reactor system at the University of Southampton (UK), with pre- (right) and post-(left) treatment solution of 100mg/L Co^{2+} and 500mg/L EDTA (500 ml flasks), adjusted to pH 12 to simulate evaporator concentrates. Co-EDTA solution was treated for 30 mins, at 112.4 mA and 0 .68kV. The dark brown suspension present following treatment was identified as cobalt oxide or cobalt (oxy)hydroxide via ICPMS. Energy consumed during treatment was 0.04 kWh. Authors' unpublished data.

2. Methods

2.1. Target LRWs

Target LRWs consisted of legacy wastes from the Chornobyl NPP catastrophe in 1986, specifically LRW from settling tanks of the Sanitary Treatment Object (STO) “Dibrova” (literally “Oakwood Forest” in Ukrainian) of the Specialised State Enterprise “Central Enterprise for Radioactive Waste Processing” (SSE “CERWP”) (Fig. 2a). The Dibrova STO contains tailings and drain water (mostly water from uncontrolled discharges and leaks) from Chornobyl Building № 5, and deactivation solutions applied to vehicles and cargo used in the liquidation efforts following the Chornobyl NPP disaster. The settling tanks of the Dibrova STO comprise two equal-size independent sections constructed from reinforced concrete, with reinforced concrete slabs and access covers (Fig. 2b). Their total volume is 1097 m^3, consisting of four compartments for (i) sludge settling (volume 330 m^3), (ii) coagulation (135 m^3), (iii) filtration (via a clinoptilolite filter, compartment volume 65 m^3) and (iv) a container compartment for the resulting purified water (18.5 m^3).

During the 30+ years of their operation, the STO facilities have not been regularly inspected for either safety or performance efficiency, and during summer periods intense evaporation occurs, while during heavy rainfall in spring and autumn the tanks fill with rain and flood water (including in-washed organic materials). The overall impact of these

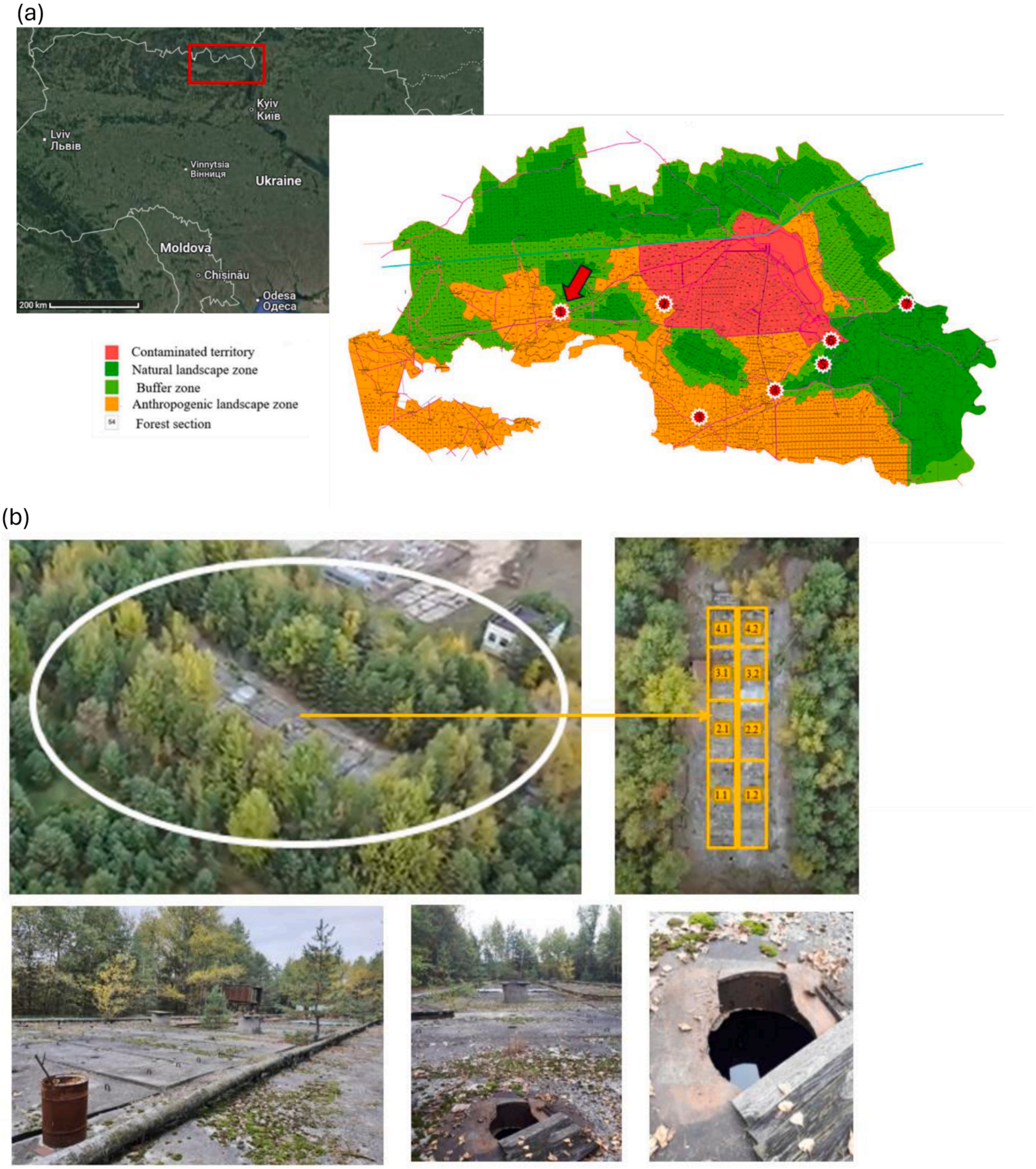

Fig. 2. (a) Location of the Dibrova Sanitary Treatment Object (STO) within the Chornobyl Radiation and Environmental Biosphere Reserve, Ukraine. Numbers refer to: 1 – STO “Dibrova” (marked with red arrow); 2 – military camp location in 1986 in Stechanka village; 3 – radioactively contaminated machinery location site near Rozsokha village; 4 – STO “Rudnya-Veresnya”; 5 – radioactively contaminated machinery location site near Zapillya village; 6 – radioactively contaminated areas in the town of Chornobyl; 7 – STO “Paryshiv”. Inset map: Aerial photographic imagery Copyright 2024 Google. Map data Copyright 2024 Google. (b) General view of the Dibrova Object and the settling tanks, with settling tank identification numbers (see Table 1).

processes is the dilution of the liquid wastes and oversaturation of compartments resulting in uncontrolled mixing between different compartments.

2.2. Sampling

LRW sampling, system mobilisation and demobilisation, and LRW treatment took place over five visits to the Dibrova site during the period 01.03.2020–27.12.2021. Samples of LRW were taken from all eight sections (1.1, 1.2, 2.1, 2.2, 3.1, 3.2, 4.1 and 4.2) of the settling tanks of the Object (Fig. 2b), from depths of 0.5 m (near-surface) and 4 m (close to the tank base). Activities of Cs-137 and Sr-90 in the samples before treatment is shown in Table 1.

A marked increase in activity is observed towards the settlement tank base, which is due to accumulation of denser suspended particles or flocs containing Cs-137 and Sr-90. Due to ease of access, samples from sections 1.2 and 3.2 were chosen for further experiments on LRW decontamination.

2.3. Radioanalysis

Radiometric measurements were conducted at the State Specialised Enterprise “Central Enterprise for the Management of Radioactive Waste” in Kyiv, using gamma-radiometer RKG-05P (Tensor Ltd, Dubna, Russian Federation), NaI(Tl) gamma-detector ø63×63 mm, and laboratory alpha-, beta- radiometer UMF-2000 (Norma-2020 Ltd, Dnipro, Ukraine) for measuring low-level radioactivity (using a silicon ion-implanted detector, area 500 mm^2).

2.4. Non-thermal plasma system set-up and operation

A team from the Institute of Environmental Geochemistry of the National Academy of Sciences of Ukraine (further IEG) organised three trips to the Object site in the Chornobyl Exclusion Zone (ChEZ) to install and assess the efficiency of the system for LRW treatment and optimise its working parameters. A modular system design was used for mobility and ease of transportation, with testing carried out on-site. The major requirements for LRW decontamination (and so system design) were:

1. decontamination of radioactive nuclides (^{90}Sr, ^{137}Cs, ^{241}Am, and others present at trace activities);
2. removal of suspended materials (rust, clay, fine sand, etc.), nanodispersions and colour;
3. use of inexpensive natural and modified sorbent materials (such as bentonite, zeolite or palygorskite) and nanocomposites;
4. synergetic action and integration of plasma chemistry with subsequent sorbent stages;
5. treatment in situ, for further processing and disposal.
6. possibility of post-treatment deactivation of the equipment.

Table 1
Activity of Cs-137 and Sr-90 in LRW samples taken from the Object “Dibrova”.

Section #	Depth of sampling, m	Activity, Bq/L	
		Cs-137	Sr-90
1.1	0.5	15	2
	4	345	458
1.2	0.5	4	2
	4	272	485
2.1	0.5	23	12
	4	308	542
2.2	0.5	33	0
	4	321	512
3.1	0.5	18	4
	4	270	534
3.2	0.5	18	6
	4	250	628
4.1	0.5	29	0
	4	312	452
4.2	0.5	24	0
	4	325	493

The plasma reactor for LRW treatment formed the core of the treatment system (Fig. 3), and consisted of a high voltage power source, flow-through reactor and erosion resistant (stainless steel) electrodes. To maintain an effectively 3-D plasma throughout the reactor vessel, metal granules (4 – 5 mm dimension) were added which create microelectric discharges upon contact with each other in a water flow. Previously copper and iron granules were tested in different plasma reactors; both metals showed similar results (authors’ unpublished data), and in the experiments with LRW described here iron granules were utilised. The metal granules serve two purposes: being electric conductors they act as microelectrodes for volumetric plasma generation in the reactor, and during electric discharge they release fine metallic particles (characterised and described in Supporting Information, SI) capable of adsorbing some radionuclides. Hydrodynamic cavitation and vortex aeration units are also built into the treatment process to (a) generate pressure pulses which initiate the formation and breakdown of microbubbles in the treated LRW and the plasma reactor, (b) cause ozonation in the microbubbles, aiding the breakdown of organic constituents, and (c) generate eddies which accelerate coagulation and allow centrifugal separation of suspended particles. Additional sorbents and ion exchangers are used in other units as described below.

The overall modular treatment process was as follows:

LRW samples were adjusted with 8 % NaOH aqueous solution to pH 9.0–9.5, and then placed in 100-L containers. The LRW was then pumped through the non-thermal plasma reactor, removing organic contaminants and ligands/complexants, and releasing metallic particles (characterised and described in SI) from the iron granules suspended in the plasma reactor in a fluidised state (Fig. 4). The insoluble products of the plasma oxidation and mechanical suspension were removed by filtration, and then a sorbent material (bentonite, “Obvazhuvachiv” Ltd, Konstyantynivka, Ukraine, 150–200 g per 10 L of liquid)) was mixed in with the treated liquid. The liquid-sorbent mixture was then pumped into a hydrodynamic cavitator. In the cavitator, the liquid-sorbent mixture is vigorously mixed (cavitation reduces the volume of required sorbent in comparison with mechanical mixing), and then pumped into a sorption column, into which a flocculant (PAA-GS, grade A anionic, consisting of 56 % polyacrylamide, 34 % ammonium sulphate 34 %, and 10 % water) and zeolite (3 – 3.5 kg) were added. The liquid and the solids were separated in the column by precipitation. The solid residue was removed from the liquid phase by pressing through a filter and the liquid was transferred into the aerator which saturated it with air. Finally, the liquid was purified by ultrafiltration, after which its composition satisfied the local requirements for wastewater discharge (Fig. 4, discussed further below).

The technical system characteristics are summarised in Table 2.

Initially, the system was assessed over a plasma voltage range of 500 – 900 V, and pulse frequency of 10 – 400 Hz, with varying liquid residence times in the hydrocavitation and acoustic-vortex aeration units. Optimal parameters for system performance were a plasma voltage of 580–600 V and pulse frequency of 180–190 Hz in the non-thermal plasma reactor, and a flow rate through the hydrodynamic cavitator in a recycling flow regime of 15–20 L/h at pressure 3.5 bar. These conditions were used for the experiments detailed and reported below.

3. Results

The liquid volume treated in each cycle in the plasma reactor was 10 L. In total, 2m^3 of LRW were processed, using a cycling/recycling mode through the plasma reactor. Three decontamination regimes were run for each sample, a short initial run of the full treatment system (15 mins duration, Experiment 1, to observe and record system operation),

Fig. 3. Upper panel: Left: General view of the assembled treatment system. Key components are numbered as follows: 1 – water pump; 2 – plasma treatment unit (with plasma reactor inside); 3 – filtration unit; 4 – container with concentrated LRW; 5 – microbubble aerators; 6 – outlet filtration unit; 7 –electronic plasma control unit. Right: detail of the non-thermal plasma flow-through reactor (transparent walls show the iron granules loaded into the reactor). Lower panel image shows the plasma reactor in operation. The internal diameter of the plasma unit is 40mm.

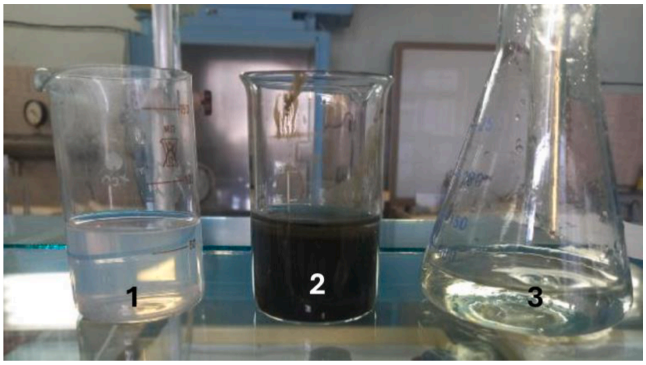

Fig. 4. Liquid radioactive waste samples: 1 – before plasma treatment; 2 – after plasma treatment with suspended iron-rich particles; 3 – purified treated water (after final filtration).

Table 2
Technical characteristics of the modular LRW treatment system.

Technical parameter	System operating characteristics
Electrical safety	Ukraine national standards of safety for electrical equipment
Electrical supply	220/380 V, 50 Hz electricity supply
Power	1 kW
Power consumption	Not exceeding 10 kW (per hour)
Working pressure	0.2 MPa
Air consumption	Air consumption per 1 m^3 of purified liquid – 3 m^3
Electric discharge pulse frequency	1 – 100 Hz
Consumables (sorbent materials)	<1 % v/v of the liquid treated
Treatment volume	No less than 10 L/h
Residue separation	Ability to separate purified water from the solid (friable) residue
Operation	Continuous operation – at least 8 h
Weight	<50 kg

followed by full duration (45 mins) runs with (Experiment 2) and without (Experiment 3) additional filtration and membrane separation. Experiment 2 was run in automatic mode (testing the ability of the system to be operated remotely, in areas with higher radiation dose), while experiment 3 was operated in manual (i.e. operator-present) mode. For lower activity LRW samples taken from the near-surface of the Dibrova waste compartments, each of the three decontamination regimes effectively removed Sr-90 (Table 3). For Cs-137 removal, additional filtration at the final treatment stage in both automatic and manual regimes was required to eliminate this radionuclide completely (i.e. to below detection limits) from the liquid. For the higher activity sample collected near to the base of the waste compartments (with initial activities of 75 Bq/kg (Cs-137) and 195 Bq/kg (Sr-90)), the effect of the treatment was similarly pronounced, with >90 % purification for both Cs-137 and Sr-90 (Table 4).

The chemical composition and other water quality parameters of the samples after treatment were also analysed for their compliance with local water quality guidelines for sewage discharge (Table 5). Of particular note here is the effective removal of:

(a) nitrite and phosphate (removal rates of ca. 99 % and >60 % respectively). The former is most likely due to oxidation to nitrate via ozonation and other oxidative reactions in the plasma reactor (e.g. Lin and Wu, 1996), the latter due to immobilisation by the suspended and coagulated Fe (hydr)oxides (e.g. Xie et al., 2023) which were generated by the iron granules in the nonthermal plasma reactor (see Supporting Information);
(b) COD (reduced by >95 %, due to oxidation reactions in the plasma reactor); and
(c) total dissolved solids (TDS), which were reduced by ca. two-thirds (note change in units in Table 5).

According to Ukrainian national legislation, the water composition satisfied the criteria of the “Rules for accepting wastewater into the central drainage system” and could be discharged directly into sewage.

After the complete cycle of decontamination by the modular system, a solid residue of ca. 100 g was obtained from 10 L of LRW (consisting of Fe, and Fe oxides and hydroxides, released from the iron granules used in the plasma reactor (SI), and coagulated suspended and colloidal particles and (co)precipitates). Upon drying, its weight reduced to 56 g. Data for the activity of Cs-137, Sr-90 and other radionuclides in this solid residue are shown in Table 6.

Both Cs-137 and Sr-90 have clearly significantly concentrated in the solid residue, at activities greater than 40 kBq/kg. Am-241, Eu-154, Co-60, and Nb-94 were not detected in the initial liquid samples due to their low activities in the LRW. During the various decontamination stages these radionuclides however concentrated in the solid phase residue and became readily detectable, particularly Am-241 which was measured at over 2 kBq/kg in the residual solid. The MAL (Maximum Allowed Level) for Am-241 in water is 70–80 Bq/L. In this case the total activity of Am-241 in the solid residue corresponds to the 10-L volume of LRW. Therefore, the total activity of Am-241 was $2182\times0.056 = 122$ Bq/kg solid, or 12.2 Bq/L (in the 10 L LRW volume), well below its MAL.

Table 3
Decontamination of near-surface LRW sample (Sample 1 Section 1.2, volume 10 L) from the Dibrova waste compartments.

Treatment	Activity, Bq/kg			
	Cs-137	Error, %	Sr-90	Error, %
Initial	15.5	50	2	50
Experiment 1 – Full treatment cycle	16.4	50	0	0
Experiment 2 – Full treatment cycle (filter + membrane)	0	0	0	0
Experiment 3 – Full treatment cycle (manual regime)	0	0	0	0

Table 4
Decontamination of near-bottom LRW sample (Sample 2 Section 3.2, volume 10 L) from the Dibrova waste compartments.

Treatment	Activity, Bq/kg			
	Cs-137	Error, %	Sr-90	Error, %
Initial	75	36	195	26
Experiment 1* - Full treatment cycle	9	100	33	67
Experiment 2 – Full treatment cycle	0	0	7	100
Experiment 3 – Full treatment cycle	6.6	100	0	0

[*] The higher residual activities of radionuclides in Experiment 1 are due to the shorter duration of this experiment: it was used to record a short video of the plasma decontamination process in real time and so each step was shorter than the optimal duration.

4. Discussion

4.1. Treatment effectiveness

The pilot non-thermal plasma-based system tested proved to be an efficient and effective method for the decontamination of multicomponent liquid radioactive wastes (LRW) derived from the Dibrova Sanitary Treatment Object, Chornobyl region, Ukraine. The removal of Cs-137 and Sr-90 from lower activity LRW near the surface of the Dibrova storage tanks reached almost 100 %, although the removal of these radionuclides from highly active LRW near the bed of the tanks was slightly less efficient (but still exceeded 90 %). To achieve even higher removal efficiencies for Sr-90 would require revising the technological parameters of the treatment system (including to incorporate longer treatment times) and potentially including a more effective sorbent than the bentonite/zeolite mix utilised here. Cs-137 was removed efficiently by the treatment system even though ferrocyanide materials (which are considered as sorbents of choice for selectively binding this radionuclide, e.g. Toropov et al., 2014) were not applied. Treatment efficiencies for other waste components (e.g. nitrites, phosphates and COD) are equivalent to or exceed those previously reported for treatment of other environmental liquid wastes by similar Advanced Oxidation Processes (e.g. landfill leachate, see comprehensive review and data in Deng and Zhao, 2015). The power requirements of the system (due to the pulsed nature of the plasma generated) were relatively low, at 10 kWh, for a LRW treatment rate of 15 - 20 L/h. The treatment process has low chemicals usage and yielded minimal solid treatment residues/sludges (here, 56g dry mass), in comparison to for example Fenton-based processes (Deng and Englehardt, 2006). In addition, the low masses of solid residue generated during the treatment process can be readily disposed via existing solid disposal routes (see below). The system can be operated remotely in autonomous mode, and its modular, easily transportable nature means that it can be readily adapted for various on-site waste treatment scenarios.

4.2. Conformance of treated LRW with disposal or discharge limits

Both the physicochemical and radiological parameters of the decontaminated water satisfy the criteria for wastewater discharge into the centralised sewage system adopted by the Ministry of Communities and Territories Development (Ukraine), Order № 286 from 09.11.2021. The key criteria in this Order are: COD < 80 mg/L; pH 6.5–9.0; and TSS (total suspended solids) < 15 mg/L. In terms of residual radioactivity, according to the national standard NRBU-1997, Cs-137 should be < 100 Bq/L and Sr-90 < 10 Bq/L. Based on the data shown in Tables 3-5 the decontaminated water from the LRW stored at the Object “Dibrova” could be reused again or discharged into the centralised sewage system for further treatment at a Wastewater Treatment Plant.

For solid phase materials, the radioactivity measurements in the solid (friable) residue of the LRW treatment (Table 6) showed that (a) the activity of α-emitting radionuclides was in the range of 0.1 to 6.0

Table 5

Water parameters before (a) and after (b) non-thermal plasma treatment (full treatment cycle). Note that only some parameters were measured prior to non-thermal plasma treatment due to the high radioactivity and consequent need for limited handling of the LRW material.

(a)

Parameter	Unit	Value	MAL*	Measurement method, national standard or ISO	Error, δ, Δ P=0.95
Sample #2 (ref. Table 4)					
TDS**	mS/cm	7.8		conductivity	
Hydrocarbonates	mg/dm^3	150		photocolorimetry	δ = ± (3–20) %
Alkalinity	mg/dm^3	0.06		ISO 9963–1:2007	δ = ± (3–20) %
Hardness	mg/dm^3	25		ISO 6059:2003	δ = ± (3–20) %
Ca^{2+}	mg/dm^3	13		titrimetry	δ = ± 12 %
Mg^{2+}	mg/dm^3	6.5		titrimetry	δ = ± 12 %
Sulphates	mg/dm^3	390	400	titration with barium chloride	Δ =±(3–10) mg/dm^3
Nitrites	mg/dm^3	50	0.8	photocolorimetry with Griess reagent	δ = ±(20–25)%
Phosphates	mg/dm^3	2.5	5.0	photocolorimetry with ammonium molybdate	δ = ±(20–10)
COD	mg/dm^3	970	80	titration	δ = ± (3–20) %

(b)

Parameter	Unit	Value	MAL*	Measurement method, national standard or ISO	Error, δ, Δ P=0.95*
Sample #1 (ref. Table 3)					
TDS**	µS/cm	2290		conductivity	
Hydrocarbonates	mg/dm^3	4.9		photocolorimetry	δ = ± (3–20) %
Alkalinity	mg/dm^3	0.08		ISO 9963–1:2007	δ = ± (3–20) %
Hardness	mg/dm^3	20		ISO 6059:2003	δ = ± (3–20) %
Ca^{2+}	mg/dm^3	641		titrimetry	δ = ± 12 %
Mg^{2+}	mg/dm^3	97		titrimetry	δ = ± 12 %
Sulphates	mg/dm^3	330	400	titration with barium chloride	Δ =±(3–10) mg/dm^3
Nitrites	mg/dm^3	0.096	0.8	photocolorimetry with Griess reagent	δ = ±(20–25)%
Phosphates	mg/dm^3	0.05	5.0	photocolorimetry with ammonium molybdate	δ = ±(20–10)
Fe total	mg/dm^3	0.03	3.0	photocolorimetry	Δ = ±(1.96σ(Δ^0)) δ = ±50
Cr	mg/dm^3	0.02	0.5	extraction+photocolorimetry with diphenylcarbazide	δ = ± (35–23) %
Ni	mg/dm^3	0.149	0.2	photocolorimetry	δ = ± (18–10) %
Co	mg/dm^3	0.035	0.1	AAS***	
Zn	mg/dm^3	0.79	2.5	photocolorimetry	δ = ± (40–15) %
Sample #2 (ref Table 4)					
TDS**	µS/cm	2570		conductivity	
Hydrocarbonates	mg/dm^3	6.1		titrimetry	δ = ± (3–20) %
Alkalinity	mg/dm^3	0.1		ISO 9963–1:2007	δ = ± (3–20) %
Hardness	mg/dm^3	24		ISO 6059:2003	δ = ± (3–20) %
Ca	mg/dm^3	721		titrimetry	δ = ± 12 %
Mg	mg/dm^3	146		titrimetry	δ = ± 12 %
Sulphates	mg/dm^3	315	400	titration with barium chloride	Δ =±(3–10) mg/dm^3
Nitrites	mg/dm^3	0.056	0.8	photocolorimetry with Griess reagent	δ = ±(20–25)%
Phosphates	mg/dm^3	0.94	5.0	photocolorimetry with ammonium molybdate	δ = ±(20–10)
COD	mg/dm^3	30	80	titration	δ = ± (3–20) %
Fe total	mg/dm^3	0.83	3.0	photocolorimetry	Δ = ±(1.96σ(Δ^0)) δ = ±50
Cr	mg/dm^3	0.13	0.5	extraction+photocolorimetry with diphenylcarbazide	δ = ± (35–23) %
Ni	mg/dm^3	0.04	0.2	photocolorimetry	δ = ± (18–10) %
Co	mg/dm^3	0.19	0.1	AAS	
Zn	mg/dm^3	0.4	2.5	photocolorimetry	δ = ± (40–15) %

[*] MAL – maximum allowed level (Ukrainian national legislation).

[**] TDS – total dissolved solids.

[***] AAS – atomic absorption spectrometry.

Table 6

Activity of radionuclides in the solid residue, weight 56 g.

Activity, Bq/kg Error, %											
Cs-137	%	Am-241	%	Eu-154	%	Co-60	%	Nb-94	%	Sr-90	%
40,339	8.0	2182	11	83	8.0	47	9.0	9.1	15	43,374	11

kBq/kg; and (b) the activity of β- and γ-emitting radionuclides was in the range of 10.0 to 5000 kBq/kg. These parameters satisfy the requirements of the State Service of Ukraine for Emergency Situations according to its official Act “Criteria for accepting radioactive wastes for disposal at the Storage Site of Radioactive Wastes “Buryakivka” adopted in 2011. The solid residue of the LRW treatment is therefore within permitted limits that would allow it to be stored subsequently at the licenced Storage Site “Buryakivka”.

5. Conclusions

- The pilot modular non-thermal plasma-based system proved to be an efficient and effective method for the decontamination of multi-component liquid radioactive wastes (LRW) derived from the Dibrova Sanitary Treatment Object, Chornobyl region, Ukraine. >90 % of Cs-137 and Sr-90 contamination was removed, producing a low mass (solid) contaminated residue.

- The concentration of various water contaminants was significantly reduced after the treatment, with major water quality parameters such as COD and nitrite and phosphate concentrations reducing by 3–5 times. The decontaminated water satisfied the criteria for discharge into the centralised sewage system for processing at a Wastewater Treatment Plant, or for reuse for technical applications.
- The solid (friable) residue separated from the LRW contained the α-, β- and γ-emitting radionuclides Am-241, Cs-137, Sr-90, Eu-154, Nb-94 and Co-60, of which only Cs-137 and Sr-90 were detected in the initial LRW samples. The other radionuclides were present at activities below detection limits. While these radionuclides have clearly concentrated in the solid residue produced by the treatment system, their activities in the solid residue still satisfied the criteria for storage at the Storage Site of Radioactive Wastes "Buryakivka" in the Chornobyl Exclusion Zone, providing an effective onward waste management route.
- Overall, we demonstrate use of this modular system on-site, using real LRW materials, at TRL 5/6. System operational parameters at this TRL include: Water treatment capacity of 120 L per day (for an 8-hour working period); Separation of solid and liquid phases at a ratio of 1:100; Decontaminated water satisfies the criteria for its discharge into the centralised sewage system; Power consumption of 10 kWh; Ability to work autonomously without the need for operator control; and satisfaction of national health and safety requirements for equipment operation and for instruments used for handling radioactive wastes.
- Based on these promising pilot trial results, further trial work, on-site deployments and supporting laboratory studies are needed to optimise system performance for different LRW types and radionuclides (particularly for more complex (and concentrated) mixed organic-radionuclide liquors and slurries) both in the Chornobyl Exclusion Zone and at other nuclear and radioactively-contaminated sites. More widely, and for larger-scale application, the system and plasma stability, efficiency and power consumption for longer treatment times and larger waste volumes requires assessment, including for higher volume lower activity liquid wastes and for non-nuclear waste treatment applications (e.g. for larger volume leachates and industrial and / or mining discharges, and process waste waters).

CRediT authorship contribution statement

Yuriy Zabulonov: Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Sergey Shpilka:** Investigation. **Danylo Tutskyi:** Investigation. **Sergey Mikhalovsky:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Formal analysis, Conceptualization. **Matthew Illsley:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition. **Alistair Shokat:** Writing – review & editing, Investigation. **Andrew B. Cundy:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Sergey Mikhalovsky reports financial support was provided by European Union. Matthew Illsley reports financial support was provided by European Union. Andrew B. Cundy reports financial support was provided by Engineering and Physical Sciences Research Council. Andrew B. Cundy reports financial support was provided by Higher Education Innovation Fund. Sergey Mikhalovsky reports a relationship with Anamad Ltd. that includes: board membership, employment, and funding grants. Matthew Illsley reports a relationship with Anamad Ltd that includes: board membership, employment, and funding grants. Yuriy Zabulonov has patent #NL2021149B1 issued to Indra Scientific SA (Belgium). Yuriy Zabulonov has patent #NL2021763B1 issued to Indra Scientific SA (Belgium). Yuriy Zabulonov has patent #UA150320U issued to Alpha Atom LLC (Ukraine). If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.hazadv.2025.100646.

Data availability

Data will be made available on request.

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