

Review

Liquid Radioactive Wastes Treatment: A Review

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Abstract: Radioactive wastes are generated during nuclear fuel cycle operation, production and application of radioisotope in medicine, industry, research, and agriculture, and as a byproduct of natural resource exploitation, which includes mining and processing of ores, combustion of fossil fuels, or production of natural gas and oil. To ensure the protection of human health and the environment from the hazard of these wastes, a planned integrated radioactive waste management practice should be applied. This work is directed to review recent published researches that are concerned with testing and application of different treatment options as a part of the integrated radioactive waste management practice. The main aim from this work is to highlight the scientific community interest in important problems that affect different treatment processes. This review is divided into the following sections: advances in conventional treatment of aqueous radioactive wastes, advances in conventional treatment of organic liquid wastes, and emerged technological options.

Keywords: radioactive waste; treatment; sorption; membrane

1. Introduction

The generation of radioactive wastes varies from country to country depending on the scale of applications and range of activity associated with nuclear and radioactive material utilization in that

country. These wastes can affect human health and the environment, so their safe management has received considerable attention worldwide. Classification of these wastes is very helpful through out their management phases from generation through collection, segregation, treatment, conditioning, storage, transportation to final disposal. Classifications are usually derived from different perspectives, *i.e.*, safety perspective, the physical/chemical characteristics of the waste, process engineering demands or regulatory issues [1,2]. The radioactivity level in the waste affects the selection of its different management options owing to its shielding requirements, so the current internationally accepted classification system is based on the activity level and half life. This system classifies the radioactive wastes to exempt (EW), low- and intermediate-level wastes (LILW), which may be subdivided into short-lived (LILW-SL) and long-lived (LILW-LL) wastes, and high-level wastes (HLW). Table 1 lists the characteristics of these waste classes [2].

Table 1. Radioactive waste classification [2].

Waste classes	Typical characteristics
EW	Activity levels at or below clearance levels, which are based on an annual dose to members of the public of less than 0.01 mSv
LILW	Activity levels above clearance levels] and thermal power below about 2 kW/m ³
LILW-SL	Restricted long lived radionuclide concentrations (limitation of long lived alpha emitting radionuclides to 4,000 Bq/g in individual waste packages and to an overall average of 400 Bq/g per waste package)
LILW-LL	Long lived radionuclide concentrations exceeding limitations for short lived waste
HLW	Thermal power above 2 kW/m ³ and long lived radionuclide concentrations exceeding limitations for short lived waste

Treatment is an important phase in the management of radioactive wastes, it aims to reduce the volume of generated wastes to enhance the safety and/or reduce the costs of further management phases. After the treatment phase, the wastes split to two portions, the first is a small volume of concentrate that contain the bulk of radionuclides that is kept in the management system and the second is a large volume portion that have low radioactivity that allow its discharge to the environment after meeting the regulatory requirements [3]. To facilitate the management of liquid radioactive wastes, they were categorized to aqueous and organic liquid wastes.

Treatment of radioactive liquid wastes is receiving considerable attention worldwide due to the recognition of its importance for the protection of human health and the environment from the adverse effect of radiation associated with these wastes [4]. Conventional treatment options are usually used to treat liquid radioactive wastes after the consideration of their chemical and biological characteristics. Recently, some trends that influence the selection and application of radioactive waste management strategy and technology have emerged worldwide. These trends includes issue of new legislation and regulations, new waste minimization strategies, strengthen the quality assurance procedures, increased use of safety and risk assessment physical protection and safeguards measures in the design and operation of waste management facilities, and new technological options. The aim of this review is to present advances in the utilization of conventional treatment technology in the management of aqueous and organic liquid wastes and highlight the emerged technological options for the management of liquid wastes. This review will cover the literature published within the last three years on topics

related to liquid waste management to highlight the scientific community interest in important problems that affect the treatment process. Finally recommendations will be drawn that identify knowledge gaps and needed research area in this field.

2. Advances in Conventional Treatment of Aqueous Radioactive Wastes

Aqueous liquid radioactive waste is generated during nuclear reactor operations and during industrial and institutional application of radioisotopes. The chemical compositions and radioactivity levels of the generated wastes depend on the conducted operation. Table 2 lists the sources of aqueous radioactive waste and its characteristics [5]. Aqueous wastes containing short lived beta/gamma activity are kept in storage. After decay to exclusion limit, if these wastes met the regulatory requirements on chemical and biological hazards they can be safely discharged into the environment. Aqueous wastes that have higher radioactivity content and/or long lived radionuclides may be treated using ion exchange/sorption, chemical precipitation, and/or evaporation, reverses osmosis, filtration and solvent extraction. The Main features and limitation of these treatment processes are shown in Table 3 [6].

Table 2. Sources of aqueous liquid radioactive wastes [6].

Source	Typical radioisotopes	Characteristics
Nuclear research centers	Might include relatively long lived, mixed with short lived	<ul style="list-style-type: none"> • Generally uniform batches with nearly neutral pH from regeneration of ion exchange resins
Radioisotopes Lab. production	Wide variety depending upon production and purity of targets.	<ul style="list-style-type: none"> • Small volumes of high specific activity and high chemical concentrations • Larger volumes of low specific activity
Radio-labeling and radiopharmaceuticals	^{14}C , ^3H , ^{32}P , ^{35}S , ^{125}I	<ul style="list-style-type: none"> • Small volume of predictable chemical composition
Medical diagnosis and treatment	^{99}Tcm , ^{131}I , ^{85}Sr	<ul style="list-style-type: none"> • Large volumes of urine from patients • Small volumes from preparation and treatment
Scientific research	Variable, with short and long lived radioisotopes	<ul style="list-style-type: none"> • Extremely variable
Industrial and pilot plants	Depends upon application	<ul style="list-style-type: none"> • Volumes could be large and chemical composition undefined
Laundry and decontamination	Wide variety likely	<ul style="list-style-type: none"> • Large volumes with low specific activity but containing complexing agents

Table 3. Features and limitation of different aqueous liquid treatment options [5].

Technology	Features	Limitations
Precipitation	<ul style="list-style-type: none"> • Suitable for large volumes and high salt content waste • Easy non-expensive operations 	<ul style="list-style-type: none"> • Low DF • Efficiency depends on solid-liquid separation step
Ion –Exchange	<ul style="list-style-type: none"> • Good chemical, thermal and radiation stability • Large choice of products ensuring high selectivity 	<ul style="list-style-type: none"> • Affected by high salt content • Blockage problems • Regeneration and recycling often difficult employed
Evaporation	<ul style="list-style-type: none"> • *DF > 10⁴ to 10⁶ • Well established technology • High volume reduction factor • Suitable for a variety of radionuclides 	<ul style="list-style-type: none"> • Process limitations (scaling, foaming, corrosion, volatility of certain radionuclides) • High operation and capital costs
Reverse osmoses	<ul style="list-style-type: none"> • Removes dissolved salts • DF 10²–10³ • Economical • Established for large scale operations 	<ul style="list-style-type: none"> • High pressure system, limited by osmotic pressure • Non-back washable, subject to fouling
Ultrafiltration	<ul style="list-style-type: none"> • Separation of dissolved salts from particulate and colloidal materials • Good chemical and radiation stability for inorganic membranes 	<ul style="list-style-type: none"> • Fouling • Organic membranes subject to radiation damage
Microfiltration	<ul style="list-style-type: none"> • High recovery (99%) • Low fouling when air backwash 	<ul style="list-style-type: none"> • Sensitive to impurities in waste stream
Solvent extraction	<ul style="list-style-type: none"> • Selectivity enables removal, recovery or recycle of actinides 	<ul style="list-style-type: none"> • Generates aqueous and organic secondary waste

* DF is the decontamination factor.

2.1. Ion Exchange/Sorption

By the beginning of the nuclear industry, the utilization of ion exchange procedures in water and wastewater treatments was well developed. Various recent studies were devoted to prepare and examine new ion-exchangers that can challenge some difficulties accompanied the industrial application of this treatment option and to improve its performance. Composite materials are an example of these tested new ion-exchangers, they consist of one or more sorbents combined with another material. Composite can be inorganic or organic and may be a sorbent. The produced material is granular with sufficient strength for column use from sorbents that do not form or only form weak, granules. This section will summarize recent researches devoted to prepare, characterize and test new sorbent materials.

The selection of ion exchanger is strongly affected by the chemical composition of the waste water. This effect was studied by conducting combined static and dynamic adsorption experiments for the removal of uranium from aqueous waste [7]. These experimental results showed that the efficiency of the studied resin was reduced in the presence of anions, triethanolamine and oil in the waste stream. The study suggested that the maximal allowable concentration of triethanolamine through the resin should not exceed 250 mg/L. Also, it was found that when oil content in the resin exceeded 11%, the breakthrough volume almost lost at all.

Removal studies to assess cobalt, cesium, and strontium radionuclides uptake have received continued attention. Removal of Co, Sr and Cs from radioactive laundry wastewater generated from Nuclear Power Plants (NPP) was investigated using ammonium molybdophosphate-polyacrylonitrile (AMP-PAN) by studying single- and bi-solute competitive adsorptions [8]. The results of single adsorption model analyses showed that AMP-PAN has high selectivity for Cs and its maximum adsorption capacity was calculated. The results of bi-solute competitive adsorptions indicated that the adsorption suppressed by the presence of competing metal ions and the presence of cationic (OTMA and HDTMA) and anionic surfactants (SDBS and SOBS) for all studied radionuclides. In another study, the uptakes of Cs, Co and Sr ions onto nano-crystalline silicotitanate (IONSIV™ IE-91 1, UOP) were investigated using batch technique [9]. The analysis of the equilibrium sorption characteristics was performed and sorption capacity for the studied radionuclides onto the silicotitanate was calculated using Langmuir model at different pH. The results indicated that silicotitanate was highly selective for Cs.

Ion exchange properties of zeolites have received great attention, especially for application in radioactive liquid waste treatment. The cationic radioisotopes, present in the liquid effluents of low and intermediate level liquid wastes, can be removed by the ion exchange with the Na⁺ ions of the zeolites. These inorganic materials possess high exchange capacity, possible selectivity and specificity, good resistant to radiation [10-23]. Recently, Zeolite A was synthesized and evaluated, as inorganic ion exchange material, for the removal of Cs and Sr ions from aqueous solutions in both batch and fixed bed column operations [24]. The results showed that the total metal ion uptake and the overall bed capacity decreased by increasing the flow rate and increased by increasing initial ion concentrations and bed depth. The sorption rate constants were found to increase with the increase in flow rate indicating that the overall system kinetics was dominated by external mass transfer in the initial part of the sorption process in the column. In another study, the removal of Cs ions for aqueous solution by synthetic Na A-X zeolite was tested [25]. The zeolite blend was synthesized from fly ash using two-step method. Then the sorption potential of prepared material for the removal of Cs ions has been investigated. The results showed that synthetic zeolite blend has a promising sorption behavior.

Insoluble transition metal hexacyanoferrates have been known for decades as effective agents for the removal of radionuclides from waste solution [26]. A two-step method for the preparation of porous composite beads composed of potassium titanium hexacyanoferrate (PTH) and silica was proposed by Liu *et al.* [27]. At the first step, amorphous titania was grafting onto the wall of pores in silica bead support, then the tinania inside the pores was converting into PTH. The prepared material was characterized and the results showed that the PTH layer is coated successfully onto the wall of pores in silica bead. Finally the sorption behavior of Cs onto the prepared material was tested, it was found that the material exhibit high Cs removal ability and high distribution coefficient under high acidity and salinity conditions. Also, the feasibility of using potassium cobalt hexacyanoferrate (PCH)/SiO₂ composite as a granulated inorganic adsorbent to remove Cs from the radioactive waste solution was recently studied [28]. The PCH particles were prepared then they were stabilized into in situ-generated porous silica with aqueous silica sol used as SiO₂ source. The prepared material was analyzed and the results indicated that the PCH particles and porous silica were mixed with each other homogeneously in the composite. Competitive adsorption behaviors for Cs in the presences of H, Na, and K were studied in batch experiments to determine the distribution coefficient. It was found that the

prepared composite exhibited high Cs adsorbing capacity and good Cs selectivity from the mixture of competing ions.

Composite ferrocyanide sorbents were prepared by precipitating nickel potassium ferrocyanide in the presence of various mineral supports, which included chalk, wollastonite, bentonite, clinoptilolite, diatomite, biosilica [29]. Sorption of microamounts of Cs on the finely dispersed prepared material was studied. It was found that the distribution coefficient of Cs on composite ferrocyanide sorbents was considerably higher than on nickel potassium ferrocyanide without support. The composite ferrocyanide sorbents were tested for Cs recovery from a simulated NPP bottom residue in pH range (8.5–12.0), it was found that the distribution coefficient of Cs is 2.5–3.0 times higher than on the nickel ferrocyanide precipitate throughout the examined pH range. The composite sorbent supported on biosilica was tested for treatment of real liquid radioactive waste with a total salt content of 22.0 g/dm³ to remove Cs. Another study was devoted to prepare composite ion-exchange resins by coating copper-ferrocyanide (CFC) and hydrous manganese oxide (HMO) powders on polyurethane (PU) foam [30]. Polyvinyl acetate/Acetone was used as a binder. The foam was loaded with about five times its weight with CFC and HMO powders. Then the distribution coefficients of CFC-PU foam and HMO-PU foam for Cs and Sr were estimated. Under similar conditions the HMO-PU foam showed higher capacity as well as better kinetics for removal of Sr than CFC-PU foam for Cs. A pilot plant scale study was conducted using a mixed composite ion-exchange resin bed. This study showed that about 1,000 bed volumes could be passed before attaining a decontamination factor of 10 from an initial value of 60–80. Composite ion exchange material consisting of hydrous manganese oxide and poly methyl methacrylate (PMMA) was developed for removal of Sr from aqueous radioactive waste [31]. The prepared composite material showed very good Sr adsorption properties in aqueous solutions. Lab-scale column performance study of the developed material revealed that this material could be effectively used in column operations to remove Sr from low level radioactive waste solutions.

Many natural mineral compounds, such as clays (e.g., bentonite, kaolinite and illite), vermiculite and zeolites (e.g., analcite, chabazite, sodalite and clinoptilolite), exhibit ion exchange properties. Natural zeolites were the first materials to be used in ion exchange processes. Clay materials are often employed as backfill or buffer materials for radioactive waste disposal sites because of their ion exchange properties, low permeability and easy workability. Clays can also be used in batch ion exchange processes but are not generally suited to column operation because their physical properties restrict the flow through the bed [26]. In this respect, treatment of real salt-containing low level radioactive waste from the Leipunskii Institute of Energy Physics, State Scientific Center of the Russian Federation, using natural clinoptilolite and tripoli minerals, was studied by Bogdanovich *et al.* [32]. The efficiency of sorption recovery of Cs and Sr radionuclides with finely dispersed mineral sorbents under static conditions was investigated in relation to the sorption time, pH, size of mineral granules, sorbent amount, salt content and chemical composition of solutions, and number of successive sorption steps. It was found that the studied natural sorbents can decrease the activity of treatment of the real salt-containing waste by 2–3 orders of magnitude owing to recovery of Cs and Sr. In another study, the utilization of Romanian modified clays for the treatment of radioactive liquid waste containing UO₂ ions was assessed [33]. The results indicated that the adsorption of UO₂ ions from aqueous solution depended on the concentration of uranium in simulated wastewater, on contact time and on the ratio of sorbent/solution value and that the sorption process was spontaneous and endothermic. The study

concluded that Romanian modified clays can be used for the treatment of radioactive liquid waste containing UO_2 . Also, the adsorption parameters of Egyptian yellow sand and clay towards Co and Cs were investigated by El-Sofany *et al.* [34]. The influences of changing equilibration time, initial metal concentration, solution pH, volume of aqueous solution to weight of adsorbent ratio and temperature on the removal process have been studied. The study concluded that the maximum removal capacity of clay is greater than that of yellow sand for both ions and the mean free energy in all cases in the range corresponding to ion exchange mechanism.

In Hungarian NPP, waste streams contain radioactive isotopes in ultralow concentration and inactive compounds as major components (borate 1.7 g/dm^3 , sodium-nitrate 0.4 g/dm^3 , sodium-hydroxide 0.16 g/dm^3 , and oxalate 0.25 g/dm^3). These wastes are evaporated by adding sodium-hydroxide, until 400 g/dm^3 salt content is reached. A new technology for the selective separation of the long-live radionuclides and for the partial recycle of boric acid from the evaporator bottom residue was developed [35]. The developed waste treatment system showed good selective separation of Cs from high salt concentration and strongly alkaline evaporator bottom residue.

Intermediate-level aqueous radioactive waste stream was generated during reprocessing of spent fuel, and then they were neutralized with alkali to store them in carbon steel tank. The waste was treated for ^{137}Cs recovery using specific resorcinol formaldehyde (RF) ion exchange resin. The effluent stream from the ion exchange treatment process had significant activity due to ^{106}Ru . A study was directed to investigate the possibility of using cobalt and nickel sulfides for the removal of ^{106}Ru [36]. It was found that the decontamination factor obtained when using nickel sulfides is much higher than that of cobalt.

Pb-Fe based adsorbents were synthesized to remove Mo from the high-level radioactive liquid waste by Dodbiba *et al.* [37]. The preparation was conducted by adding sodium hydroxide in mixture of 1 mol/L lead nitrate and 1 mol/L ferric nitrate aqueous solutions. The precipitate was then filtered, dried and ground to obtain a fine powder. The effect of changing the precipitation pH and calcination temperature on the final sorbent properties was studied. The experimental results indicated that the calcination temperature of the Pb-Fe based adsorbent had great influence on sorption capacity of the sorbent for Mo. It was found that when the Pb-Fe based sorbent was calcinated at $500 \text{ }^\circ\text{C}$, the sorbed concentration of Mo was the highest.

The treatment efficiency of ^{134}Cs , ^{65}Zn , ^{60}Co and $^{152-154}\text{Eu}$ was tested based on the sorption capacity of cationic exchanger (KY-2) functionalized with polystyrene sulfonic group [38]. It was found that the enhancement in decontamination factor of each radionuclide was attributed to the high sorption capacity of the cationic resin in addition to the complexation capability of the radionuclide with the different complexant existed in the waste solution. The removal percentages were around 50% for the studied radionuclides, without complexant compound. Significant enhancements of the removal percentages were obtained for ^{65}Zn , ^{60}Co and $^{152-154}\text{Eu}$ on addition of manganese sulfate.

2.2. Miscellaneous Methods

Treatment of high salinity low-level aqueous waste containing Pu and U by flocculation was studied by Ren *et al.* [39]. The results showed that Pu can be removed effectively in alkaline condition, and that flocculation of U can be improved by decreasing the pH. The removal efficiency of U was found to exceed 95.5% by adjusting the pH to 6 and adding Fe at a dosage of 100 mg/L. In a two-step flocculation experiment, it was shown that the concentration of U after the second flocculation is lower than 10 µg/L by adjusting the pH at 7.0 and adding Fe at a dosage of about 80 mg/L.

Ultrafiltration and reverse osmosis combined methods were employed for the treatment of low-level radioactive water containing Pu [40]. The system consisted of ultrafiltration module with hollow fiber membrane and reverse osmosis module with spiral membrane. The decontamination efficiency and volume concentration ratio affected by technical parameters were explored in the experiment. The results showed that the decontamination efficiency achieves 99.94% and the volume concentration ratio achieves 12.5 at pH = 10 for solution fed into the membrane separation system.

Some experiments were performed using simulated waste solutions for CANDEREM (Canadian Decontamination and Remediation Process) and CANDECON (Canadian Decontamination Process). To improve efficiency and economics of the treatment process it was proposed to treat the waste by combining the sorption of radionuclides on natural zeolites with membrane filtration. The performance of different sorbents was compared by determining the ion exchange capacity, distribution coefficients, and evaluating the sorption characteristics. The obtained results showed that the distribution coefficients of Cs on the Na-form converted materials are higher than for that of NH⁴- and H-forms [41,42].

The biosorption of U by seaweed *Sargassum filipendula* was investigated under dynamic conditions at various bed heights [43]. The results indicated that the bed height of 40.0 cm (111.9 g biomass) was the most efficient for long-term operation of the continuous system and that the effluent solutions produced were in accordance with Brazilian legislation for safe discharge of U in aqueous streams. The study concluded that the efficiency of the process increased by increasing the bed height to 40.0 cm due to changes in the transfer zone. In treatment of a real effluent, 64% of the U was biosorbed, as well as the stable heavy metals chromium, lead and barium. The essential metals calcium, magnesium, iron and manganese were not biosorbed by the seaweed, in fact, their concentrations in the solution increased due to ion-exchange mechanisms with the constituent polysaccharides of the biomass. This work illustrated that the reduction in total mass of the loaded biomass was considerable, thus facilitating storage of the contaminated seaweed.

Treatment of simulated secondary wastes from the decontamination process by semi-permeable membrane techniques were investigated by Dulama *et al.* [44]. The study showed that increased efficiencies for Cs removal were obtained by using natural zeolite in pretreatment stage and this was attributed to the special affinity of this material for Cs. The addition of powdered active charcoal was found to serve as an advanced purifying method to remove organic compounds and residual radionuclides. The analysis of the experimental data showed a decreasing of about 50% for Co isotopes subsequently to the active charcoal adsorption.

The extraction of Co(II) from thiocyanate medium by CYANEX 923 (mixture of straight chain alkylated phosphine oxides) in cyclohexane was studied [45]. It was found that the stripping percentage of Co(II) with sulfuric acid from the loaded CYANEX 923 increased with the increase in

acid concentration. The extraction of Co(II) from aqueous thiocyanate medium into emulsion liquid membrane using CYANEX 923 extractant was also studied. The influence of different parameters such as stirring speed, surfactant concentration, pH of the extractant phase, carrier concentration, internal phase stripping acid concentration, initial Co(II) concentration as well as temperature on the emulsion stability were investigated. The applicability of the emulsion liquid membrane (ELM) process using CYANEX 923 as extractant and SPAN 80 as surfactant for the removal and the concentration of Co(II) from thiocyanate solution was investigated. The results showed that it is possible to recover 95% of Co in the inner phase after 10 min of contacting time with a concentration factor of 5.

3. Advances in Conventional TREATMENT of Organic Liquid Wastes

Nuclear energy generation and some medical research facilities produce effluents containing radioactive heavy metals and complex mixtures of hazardous organic compounds and irradiated surfactants. The volume of generated organic liquid radioactive wastes is small compared to other classes of radioactive waste. Typical types of organic wastes, sources, and their characteristics are listed in Table 4 [46]. The features and limitations of different methods that are utilized in the treatment of organic liquid wastes are illustrated in Table 5 [3].

Table 4. Sources of aqueous liquid radioactive wastes [31].

Type	Sources	Characteristics
Oils	Lubricating oils, Hydraulic fluids Vacuum pump oils	These wastes contain relatively small quantities of $\beta\gamma$ -emitting radionuclides
Scintillation liquids	Non-aqueous solvents such as steroids, lipids; and Non-polar solvents such as toluene, xylene, and hexane	The level of radioactivity for this type of waste is typically about 350 MBq/m ³ .
Solvent extraction liquids	Tri-butyl phosphate, Tri- and tertiary amino-compounds.	
Miscellaneous solvents	Toluene, carbon tetrachloride, acetone, alcohols and trichloroethane. Aqueous solutions of organic acids, such as citric acid, picolinic acid, ethylene-diamine tetra-acetic acid	Dry cleaning produces small quantities of perchloroethylene and Freonwastes. The gross $\beta\gamma$ activity of this waste is usually less than about 200 MBq/m ³ .

Table 5. Organic liquid treatment options [3].

Methods	Features	Limitation
Incineration	<ul style="list-style-type: none"> • Decomposes organic nature of Waste • High volume reduction • Combined use for other waste • Eliminates infectious hazard 	<ul style="list-style-type: none"> • Secondary waste must be treated • High temperatures are required to ensure complete decomposition • Off-gas filtration and monitoring are required
Emulsification	<ul style="list-style-type: none"> • Allows embedding of liquid organic waste into cement matrixes 	<ul style="list-style-type: none"> • Low limitations for content of emulsified liquids in the cement matrix
Absorption	<ul style="list-style-type: none"> • Solidifies and immobilizes organic liquids • Simple and cheap 	<ul style="list-style-type: none"> • Suitable only for small amounts of waste

Table 5. Cont.

Methods	Features	Limitation
Distillation	<ul style="list-style-type: none"> Removes water and detoxifies the waste for direct disposal 	<ul style="list-style-type: none"> Non-universal application Technology is relatively expensive for this type of waste
Wet oxidation	<ul style="list-style-type: none"> Produce clean solvent Low temperature process Simpler than incineration Suitable for biological waste 	<ul style="list-style-type: none"> Requires storage of oxidizing agent Residue requires immobilization

Microbial treatment represents an environmental friendly approach to achieve mineralization. Characterization of liquid radioactive waste collected from a sump at a radioisotope processing facility in Cape Town, South Africa, was performed [47]. The waste sample was extracted by solid phase extraction. Samples were analyzed for the presence of polycyclic aromatic hydrocarbons (PAHs) by using High Performance Liquid Chromatography (HPLC). The results showed that there are high levels of PAHs in the wastewater exceeding the World Health Organization (WHO) recommendation for maximum values. Then biodegradation studies were conducted in batch reactors using synthetic waste containing the controlled amounts of irradiated organics in order to determine degradation rate parameters. An indigenous culture of aromatic compound degrading bacteria obtained from a landfill site was used in the batch studies. The study concluded that the degradation kinetics for PAH (polycyclic aromatic hydrocarbons) were affected by the rate of solubility of the solid phase.

Ethylenediaminetetracetic acid (EDTA) is widely used as a decontaminating agent in nuclear industry. Photocatalytic degradation of EDTA had been investigated using Degussa P-25 titanium dioxide TiO_2 as the semiconductor photocatalyst in presence of UV light [48]. The degradation of EDTA was monitored by titrimetric method using magnesium sulfate as the titrant and Erichrome black-T as indicator. The effects of various parameters such as pH, quantity of the catalyst loading, effect of H_2O_2 were studied. The presence of amides was detected in the degraded waste, and then these wastes were subjected to precipitation. Results have shown that the degradation products of EDTA did not interfere in the chemical precipitation step and gave a good decontamination factor for the treatment process compared to the radioactive liquid waste where EDTA degradation has not been carried out.

The implementation of continuous-flow hydrothermal technology for the treatment of concentrated liquid radioactive wastes was tested by Avramenko *et al.* [49]. It had been shown that hydrothermal oxidation could solve the problem of the selective extraction of transition metals radionuclides such as Co and Mn with a minimum volume of solid radioactive wastes being formed.

Ramanjaneyulu *et al.* [50] fabricated polyvinylchloride (PVC) based liquid membrane ion selective electrode (ISE) for Cs removal. Different membrane constituents were investigated to realize optimum performance of the developed ISE. It was found that the best response was observed for the membrane having 2-nitro phenyl octyl ether (oNPOE) as plasticizer and potassium tetrakis (perchloro phenyl) borate (KTPCIPB) as ion additive. Linear response over concentration range from 10^{-5} – 10^{-1} M CsCl was obtained. The Nernstian slope of the response for this membrane was 56 mV per decade for Cs with a response time less than 20 s with fairly constant response over the pH range of 3–11. The lifetime of the electrode was found to be 9 months. Finally, the concentration of Cs in two simulated high level

active waste streams was determined and results agreed well with those obtained independently employing atomic absorption spectrometry.

The Savannah River Site (SRS) is currently removing liquid radioactive waste from its Tank Farm. Integrated Salt Disposition Process (ISDP) was developed to treat waste streams that are high in Cs, Sr, and/or actinides [51]. This process is made up of two processes: actinide removal process (ARP) and modular caustic side solvent extraction (CSSX). The ARP part was responsible for the removal of Sr and actinides by using monosodium titanate (MST). The resulting slurry was filtered to remove MST loaded by sorbed Sr and actinides and entrained sludge. The filtrate was transferred CSSX process, where Cs was extracted from the radioactive waste using a customized solvent to produce a Decontaminated Salt Solution (DSS), then stripped and concentrated the Cs from the solvent with dilute nitric acid. The DSS was incorporated in grout while the strip acid solution was transferred for vitrification. In order to predict waste behavior, MST sorption to remove Sr and actinides followed by CSSX batch contact tests to verify expected Cs mass removal and concentration were tested. The results indicated that the bench scale tests were a conservative predictor of actual waste performance.

4. Emerged Technological Options

The continuous electrodeionization (CEDI) technology was used in low-level radioactive wastewater treatment to minimize radioactive wastes and energy consumptions, with Cs, Co, and Sr chosen as the typical fission products of pressurized water reactor [52]. The results showed that the CEDI has better continuous and effective operation performance compared with conventional ion exchange processes, with a removal efficiency of Sr of more than 95%. The nuclide removal efficiency decreased with increasing ratio of influent to effluent. The CEDI technology exhibited nuclide removal efficiencies from high to low in the order of Cs, Sr, and Co which was different from the conventional ion exchange.

A novel technology was developed to treat evaporator concentrates, it included a hydrothermal ($T = 250\text{--}300\text{ }^{\circ}\text{C}$ and $P = 80\text{--}120\text{ bar}$) processing of the concentrates in oxidation medium in order to destruct stable organic complexes of Co radionuclides and remove these radionuclides by oxide materials formed during such processing [53]. This method implied that Cs radionuclides contained in evaporator concentrates were removed by a conventional method through the application of one of the developed composite sorbents with ferrocyanides of transition metals used as active agents. The study showed that hydrothermal oxidation of evaporator concentrates had a number of advantages as compared to traditional oxidation methods (ozonation, photocatalytic, electrochemical and plasma oxidation). A laboratory installation was built for the flow-type hydrothermal oxidation of NPP evaporator concentrates. The obtained experimental results showed good prospects for the developed method application. On the basis of the results obtained, a pilot installation of productivity up to 15 L/hour was developed and built. The pilot tests were performed for 6 months in 2006 at first reactor unit of the Novovoronezhskaya NPP (Voronezh Region, Russia). Optimal technological regimes were determined, and estimations of the economic soundness of the technology were made. The study concluded that the application of the developed technology in the treatment system of NPP enabled to reduce substantially the volume of solid radioactive waste sent for final disposal.

5. Conclusions and Recommendations

This work aimed to highlight the scientific community interest in important problems that affect different treatment process. From this review the following conclusions could be drawn:

- (1) Most of the published work focused on studying Cs, Co, Sr, and U uptake from different real and simulated waste streams due to the high environmental impact of these radionuclides; to a lesser extent the researches studied the uptake of Zn, Eu and Pu.
- (2) Despite real radioactive wastes containing different isotopes of varying concentrations, the majority of the tested sorbent materials were conducted by using single and bi-solute competitive adsorption. There is a need to study the behavior of these sorbents for removing the potential radionuclides as a multicomponent system.
- (3) Emerged technologies studies such as continuous electrodeionization were tested on soluble alkali radionuclides; there is a need to find their economical feasibility.

References

1. International Atomic Energy Agency. *Standardization of Radioactive Waste Categories*; TRS No. 101; IAEA: Vienna, Austria, 1970.
2. International Atomic Energy Agency. *Review of the Factors Affecting the Selection and Implementation of Waste Management Technologies*; IAEA-TECDOC-1096; IAEA: Vienna, Austria, 1999.
3. Abdel-Rahman, R.O.; El-Kamash, A.M.; Ali, H.F.; Hung, Y.T. Overview on recent trends and developments in radioactive liquid waste treatment part 1: Sorption/Ion Exchange Technique. *Int. J. Environ. Eng. Sci.* **2011**, *2*, 1-16.
4. International Atomic Energy Agency. *Management of Low and Intermediate Level Radioactive Wastes with Regard to Their Chemical Toxicity*; IAEA-TECDOC-1325; IAEA: Vienna, Austria, 2002.
5. International Atomic Energy Agency. *Handling and Processing of Radioactive Waste from Nuclear Applications*; TRS No. 402; IAEA: Vienna, Austria, 2001.
6. Ren, J.S.; Mu, T.; Zhang, W.; Yang, S.Y. Effect of Ingredients in waste water on property of ion exchange resin for uranium-contained waste water treatment. *Atom. Ene. Sci. Technol.* **2008**, *42*, 38-42.
7. Park, Y.; Lee, Y.C.; Shin, W.S.; Choi, S.J. Removal of cobalt, strontium and cesium from radioactive laundry wastewater by ammonium molybdophosphate–polyacrylonitrile (AMP-PAN). *Chem. Eng. J.* **2010**, *162*, 685-695.
8. Park, Y.; Shin, W.S.; Reddy, G.S.; Shin, S.J.; Choi, S.J. Use of nano crystalline silicotitanate for the removal of Cs, Co and Sr from low-level liquid radioactive waste. *J. Nanoelectro. Optoelectro.* **2010**, *5*, 238-242.
9. Abd El-Rahman, K.M.; El-Kamash, A.M.; El-Sourougy, M.R.; Abdel-Moniem, N.M. Thermodynamic modeling for the removal of Cs⁺, Sr²⁺, Ca²⁺, and Mg²⁺ ions from aqueous waste solutions using zeolite A. *J. Radioanl. Nucl. Chem.* **2006**, *268*, 221-230.

10. El-Kamash, A.M.; Zaki, A.A.; Abd El Geleel, M. Modeling batch kinetics and thermodynamics of zinc and cadmium ions removal from waste solutions using synthetic zeolite A. *J. Hazard Mater.* **2005**, *127*, 211-220.
11. Sinha, P.K.; Lal, K.B.; Panicker, P.K.; Krishnasamy, V. A comparative study on indigenously available synthetic zeolites for removal of strontium from solutions by ion-exchange. *Radiochem. Acta* **1996**, *7*, 157-163.
12. Dyer, A.; Abdel Gawad, A.S.; Mikhail, M.; Enamy, H.; Afshang, M. The natural zeolite, laumontite, as a potential material for the treatment of aqueous nuclear wastes. *J. Radioanal. Nucl. Chem.* **1991**, *4*, 265-276.
13. Durrani, S.K.; Dyer, A.; Blackburn, R. Self-diffusion of barium and cesium cations in neutron-and gamma-irradiated high-silica zeolites and boron-zeotypes. *Zeolites* **1993**, *13*, 1-13.
14. Kotoh, K.; Nishikawa, T.; Kashio, Y. Multi-component adsorption characteristics of hydrogen isotopes on synthetic zeolite 5A-type at 77.4 K. *J. Nucl. Sci. Technol.* **2002**, *39*, 435-441.
15. Inglezakis, V.J.; Loizidon, M.D.; Grigoropoulou, H.P. Equilibrium and kinetic ion exchange studies of Pb^{2+} , Cr^{3+} , Fe^{3+} and Cu^{2+} on natural clinoptilolite. *Water Res.* **2002**, *36*, 2784-2792.
16. Barros, M.A.S.D.; Arroyo, P.A. Thermodynamics of the exchange processes between K^+ , Ca^{2+} and Cr^{3+} in zeolite NaA. *Adsorption* **2004**, *10*, 227-235.
17. Qadeer, R.; Hanif, J.; Hanif, I. Uptake of thorium ions from aqueous solutions by zeolite molecular sieves (13X type) powder. *J. Radioanal. Nucl. Chem.* **1995**, *190*, 103-112.
18. Sinha, P.K.; Lal, K.B.; Panicker, P.K.; Krishnasamy, V. A comparative study on indigenously available synthetic zeolites for removal of strontium from solution by ion-exchange. *Radiochem. Acta* **1996**, *73*, 157-163.
19. Ouki, S.; Kavannah, M. Performance of natural zeolites for the treatment of mixed metal-contaminated effluents. *Waste Manage. Res.* **1997**, *15*, 383-391.
20. Chmielewska, E.; Horvathova, A. The interaction mechanisms between aqueous solutions of ^{137}Cs and ^{134}Ba radionuclides and local natural zeolites for reaction scenario. *J. Radioanal. Nucl. Chem.* **1998**, *227*, 151-155.
21. Abdel-Rahman, R.O.; Ibrahim, H.A.; Hanafy, M.; Abdel-Monem, N.M. Assessment of synthetic zeolite NaA-X as sorbing barrier for strontium in a radioactive disposal facility. *Chem. Eng. J.* **2010**, *157*, 100-112.
22. Abdel Rahman, R.O.; Ibrahim, H.A.; Abdel Monem, N.M. Long-term performance of zeolite Na A-X blend as backfill material in near surface disposal vault. *Chem. Eng. J.* **2009**, *149*, 143-152.
23. El-Kamash, A.M. Evaluation of zeolite a for the sorptive removal of Cs^+ and Sr^{2+} ions from aqueous solutions using batch and fixed bed column operations. *J. Hazard. Mater.* **2008**, *151*, 432-445.
24. El-Naggar, M.R.; El-Kamash, A.M.; El-Dessouky, M.I.; Ghonaim, A.K. Two-step method for preparation of Na A-X zeolite blend from fly ash for removal of cesium ions. *J. Hazard. Mater.* **2008**, *154*, 963-972.
25. International Atomic Energy Agency. *Application of Ion Exchange Processes for the Treatment of Radioactive Waste and Management of Spent Ion Exchangers*; TRS No. 408; IAEA: Vienna, Austria, 2002.

26. Liu, H.D.; Li, F.Z.; Zhao, X. Preparation of high surface area porous potassium titanium hexacyanoferrate/sio₂ bead for radioactive waste water treatment. *Chin. J. Inorg. Chem.* **2008**, *24*, 1657-1663.
27. Liu, H.D.; Li, F.Z.; Zhao, X.; Yun, G.C. Preparing high-loaded potassium cobalt hexacyanoferrate/silica composite for radioactive wastewater treatment. *Nucl. Technol.* **2009**, *165*, 200-208.
28. Milyutin, V.V.; Kononenko, O.A.; Mikheev, S.V.; Gelis, V.M. Sorption of cesium on finely dispersed composite ferrocyanide sorbents. *Radiochemistry* **2010**, *52*, 281-283.
29. Rao, S.V.S.; Lekshmi, R.; Mani, A.G.S.; Sinha, P.K. Treatment of low level radioactive liquid wastes using composite ion-exchange resins based on polyurethane foam. *J. Radioanal. Nucl. Chem.* **2010**, *283*, 379-384.
30. Valsala, T.P.; Joseph, A.; Sonar, N.L.; Sonavane, M.S.; Shah, J.G.; Raj, K.A.; Venugopal, V. Separation of strontium from low level radioactive waste solutions using hydrous manganese dioxide composite materials. *J. Nucl. Mat.* **2010**, *404*, 138-143.
31. Bogdanovich, N.G.; Grushicheva, E.A.; Mishevets, T.O.; Skomorokhova, S.N.; Trifanova, E.M.; Emel'yanov, V.P.; Petrukhina, G.N.; Starkov, O.V. Recovery of ¹³⁷Cs and ⁹⁰Sr from wastewater by sorption on finely dispersed minerals under static conditions. *Radiochemistry* **2008**, *50*, 395-401.
32. Humelnicu, D.; Popovici, E.; Dvininov, E.; Mita, C. Study on the retention of uranyl ions on modified clays with titanium oxide. *J. Radioanal. Nucl. Chem.* **2009**, *279*, 131-136.
33. El-Sofany, E.A.; Zaki, A.A.; Mekhamer, H.S. Kinetics and thermodynamics studies for the removal of Co²⁺ and Cs⁺ from aqueous solution by sand and clay soils. *Radiochimica Acta* **2009**, *97*, 23-32.
34. Pázay, G.; Weiser, L.; Feil, F.; Patek, G.; Schunk, J. Radioactive Wastewater Treatment Using Selective Ion Exchangers. In *Proceedings of 1st International Nuclear and Renewable Energy Conference, INREC'10*, Amman, Jordan, 21–24 March 2010; Art. No. 5462565.
35. Sonar, N.L.; Mishra, P.K.; Kore, S.G.; Sonavane, S.; Kulkarni, Y.A.; Raj, K.; Manchanda, V.K. Treatment of ¹⁰⁶Ru present in intermediate level radioactive liquid waste with nickel sulphide. *Sep. Sci. Technol.* **2009**, *44*, 506-515.
36. Dodbiba, G.; Wu, I.C.; Kikuchi, T.; Fujita, T. Adsorption of molybdenum in nitric acid solution by using Pb-Fe based adsorbents. In *Proceedings of the 2008 Global Symposium on Recycling, Waste Treatment and Clean Technology (REWAS 2008)*, Cancun, Mexico, 12–15 October 2008; pp. 63-68.
37. Borai, E.H.; Hilal, M.A.; Attallah, M.F.; Shehata, F.A. Improvement of radioactive liquid waste treatment efficiency by sequential cationic and anionic ion exchangers. *Radiochimica Acta* **2008**, *96*, 441-447.
38. Ren, J.S.; Mu, T.; Yang, S.Y.; Zhao, Y.J.; Luo, S.Q. Treatment of high salinity low level radioactive wastewater containing uranium and plutonium by flocculation. *J. Nucl. Radiochem.* **2008**, *30*, 201-205.
39. Xiong, Z.H.; Fan, X.H.; Luo, D.L.; Wang, T.; Chen, Q. Treatment of simulated plutonium-containing wastewater by ultrafiltration-reverse osmosis technology. *J. Nucl. Radiochem.* **2008**, *30*, 142-145.
40. Dulama, M.; Deneanu, N.; Pavelescu, M.; Pasre, L. Combined radioactive liquid waste treatment processes involving inorganic sorbents and micro/ultrafiltration. *Rom. J. Physics.* **2009**, *54*, 851-859.

41. Dulama, M.; Pavelescu, M.; Deneanu, N.; Dulama, C.N. Application of indigenous inorganic sorbents in combination with membrane technology for treatment of radioactive liquid waste from decontamination processes. *Radiochim. Acta* **2010**, *98*, 413-420.
42. Rodrigues Silva, J.I.; De Melo Ferreira, A.C.; Da Costa, A.C.A. Uranium biosorption under dynamic conditions: preliminary tests with sargassum filipendula in real radioactive wastewater containing Ba, Cr, Fe, Mn, Pb, Ca and Mg. *J. Radioanal. Nucl. Chem.* **2009**, *279*, 909-914.
43. Dulama, M.; Deneanu, N.; Dulama, C.; Pavelescu, M. Experimental studies concerning the semipermeable membrane separation efficiency for ^{134}Cs , ^{137}Cs , ^{57}Co , ^{58}Co , ^{60}Co , ^{54}Mn in liquid radioactive waste. I. Treatment of secondary waste from POD decontamination procedure. *Rev. Chim.* **2008**, *59*, 544-549.
44. Gasser, M.S.; El-Hefny, N.E.; Daoud, J.A. Extraction of Co(II) from aqueous solution using emulsion liquid membrane. *J. Hazard. Mater.* **2008**, *151*, 610-615.
45. International Atomic Energy Agency. *Treatment and Conditioning of Radioactive Organic Liquids*; IAEA-TECDOC-656; IAEA: Vienna, Austria, 1992.
46. Tikilili, P.V.; Chirwa, E.M.N. Microbial degradation of recalcitrant organics from radioactive waste using indigenous cultures of naphthalene degrading bacteria. *Chem. Eng. Trans.* **2009**, *18*, 845-850.
47. Seshadri, H.; Chitra, S.; Paramasivan, K.; Sinha, P.K. Photocatalytic degradation of liquid waste containing edta. *Desalination* **2008**, *232*, 139-144.
48. Avramenko, V.A.; Bratskaya, S.Y.; Voit, A.V.; Dobrzanskiy, V.G.; Egorin, A.M.; Zadorozhniy, P.A.; Mayorov, V.Y.; Sergienko, V.I. Implementation of the continuous-flow hydrothermal technology of the treatment of concentrated liquid radioactive wastes at nuclear power plants. *Theoret. Found. Chem. Eng.* **2010**, *44*, 592-599.
49. Ramanjaneyulu, P.S.; Singh, P.; Sayi, Y.S.; Chawla, H.M.; Ramakumar, K.L. Ion selective electrode for cesium based on 5-(4~Nitrophenylazo)25,27-Bis(2-Propyloxy)26,28-Dihydroxycalix[4]Arene. *J. Hazard. Mater.* **2010**, *175*, 1031-1036.
50. Peters, T.B.; Poirier, M.R.; Fink, S.D. Processing macrobatch 2 at the savannah river site integrated salt disposition process (ISDP). *Sep. Sci. Technol.* **2010**, *45*, 1801-1806.
51. Liu, L.; Li, F.; Zhao, X.; Zhao, G. Low-level radioactive wastewater treatment by continuous electrodeionization. *Qinghua Daxue Xuebao/J. Tsinghua Univ.* **2008**, *48*, 1012-1014.
52. Avramenko, V.; Dobrzanskiy, V.; Marinin, D.; Sergienko, V.; Shmatko, S. Novel Technology for Hydrothermal Treatment of NPP Evaporator Concentrates. In *Proceedings of the ICEM2007–11th International Conference on Environmental Remediation and Radioactive Waste Management*, (PART B), Bruges, Belgium, 2–6 September 2007; pp. 1141-1146.