

COMBINED TECHNOLOGICAL APPROACH FOR TREATMENT OF LIQUID RADIOACTIVE WASTE CONTAINING ORGANIC SUBSTANCES

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This paper describes a multi step approach to treatment of mixed radioactive waste. The approach is based on parallel development of methods for removal of organic compounds and radionuclides from aqueous solutions. A novel method – a combination of ozonization and biochemical destruction – is proposed for the destruction of organic compounds in aqueous solution. Removal of the radionuclides from solution following destruction of the organics is based on selective adjustment of the chemical forms and physico-chemical properties of the radionuclide species to optimize removal efficiency.

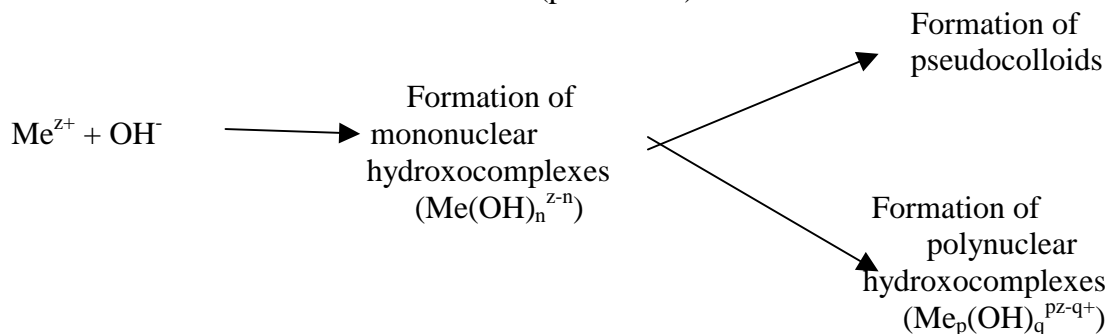
Nuclear Power Plants (NPP) operation, maintenance and decommissioning, spent fuel reprocessing, and different applications of radioactive isotopes in research, medicine and industry generate radioactive waste, some of which contain organic substances, e.g. complexing agents used in most of decontamination procedures. This waste may also contain stable metals at high concentrations, and radionuclides in varying chemical compositions. The complexity of such waste makes its treatment for disposal a difficult task.

Despite the fact that there are a number of processes used currently for the destruction of organic complexes (ozonization, chemical destruction, photocatalytic destruction, biochemical destruction, UV-destruction), and the removal of radionuclides from solution (co-precipitation, coagulation, sorption on ion-exchange materials, ultrafiltration, evaporation) there are no adequately developed technological schemes and installations for treatment of Liquid Radioactive Waste (LRW) containing substantial amounts of organic substances.

This paper describes a multistep approach to treatment of such mixed radioactive waste, based on parallel development of methods for removal of radionuclides and organic compounds from solution.

The basis of our approach to the problem of radionuclides removal from solution is to make maximum use of the physico-chemical properties of the various species, that radionuclides and stable metals can form in solution.

The following processes can occur for metal ions (Me^{Z+}) in aqueous solution as the pH increases from acidic to basic conditions (pH 1 to 11):



Each of the above forms plays a specific role in the processes used for separation of radionuclides from solution. For example, it was reported in our previous publications [1,2] that mononuclear hydroxocomplexes of Fe(III) exhibit enhanced sorption on silica gel, that is not dependent on the concentration of competitive ions. The current study shows that increases in the concentrations of inactive electrolytes even increase the sorption (for added Na^+ , Ca^{2+} - cations) or have no effect on it (added Al^{3+} -cation) (Fig.1.). This testifies to the sorption of Fe(III) mononuclear hydroxocomplexes on silica gel proceeding via a non ion exchange mechanism. An increased sorption of mononuclear hydroxocomplexes on silica gel was also observed in previous work [3].

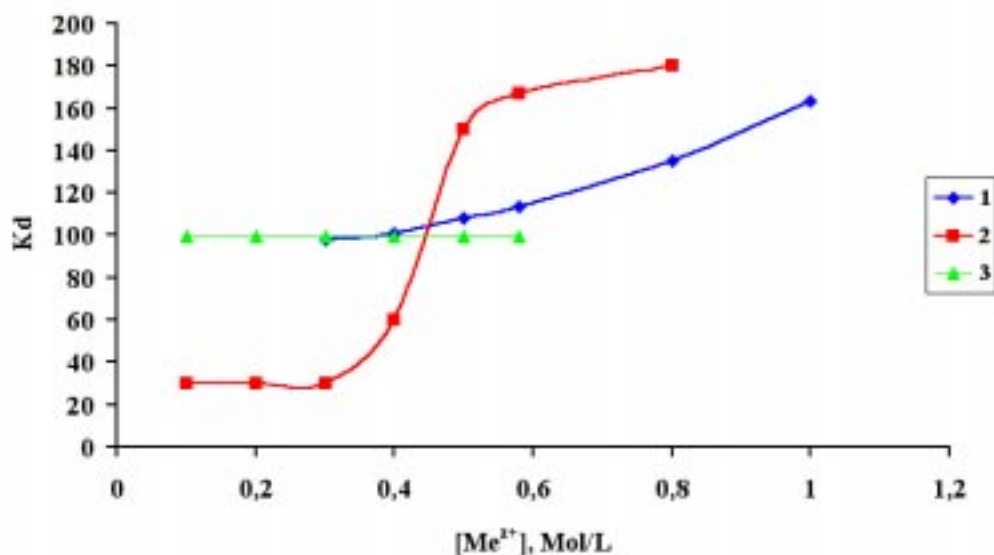


Fig.1. Dependence of Fe(III) radionuclide sorption on silica gel on concentration of inactive electrolyte in solution. pH = 2.7. 1 - Na^+ ; 2 - Ca^{2+} ; 3 - Al^{3+}

Interesting results were also obtained in the case of radionuclide sorption on cation exchange resin [2]. It has been shown that the effect of hydrolysis on the sorption of radionuclides may vary for different metal ions. Accordingly, growth of $\text{Me}(\text{OH})^{z-1+}$ hydroxocomplex concentration in solution results in a decrease of Fe(III) sorption on cation exchange resin and, at the same time, an increase in U(VI) sorption under the same conditions (Fig. 2).

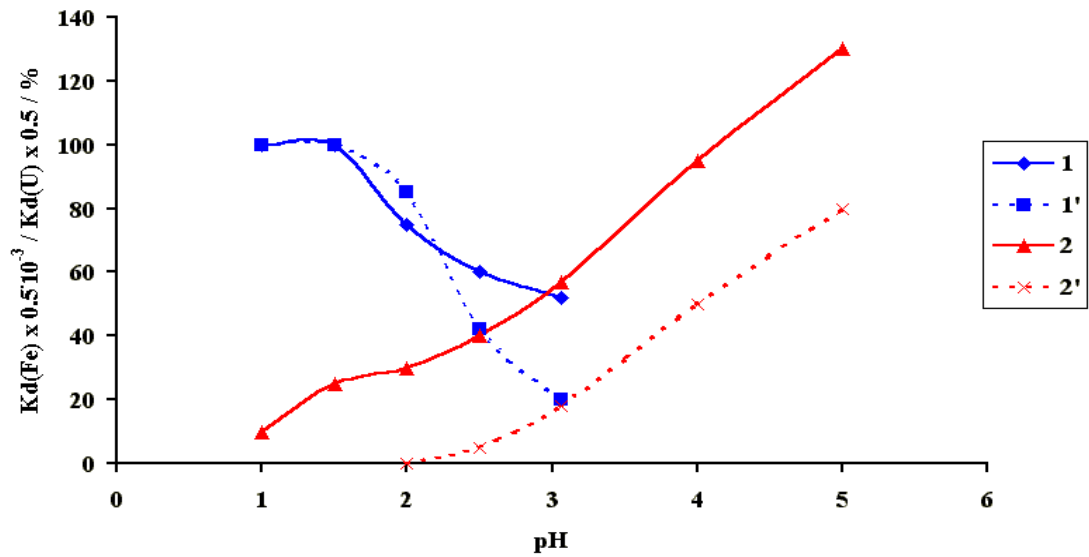


Fig.2. Sorption of radionuclides on cation exchange resin KU-2: 1 - Fe(III); 2 - U(VI); 1' - percent of Fe³⁺ -cation in solution; 2' - percent of UO₂(OH)⁺ - cation in solution

Often, authors use a stepwise complexation model to explain metal ion behavior in various processes. However, this approach can be misleading in the case of radionuclides, since, at micro

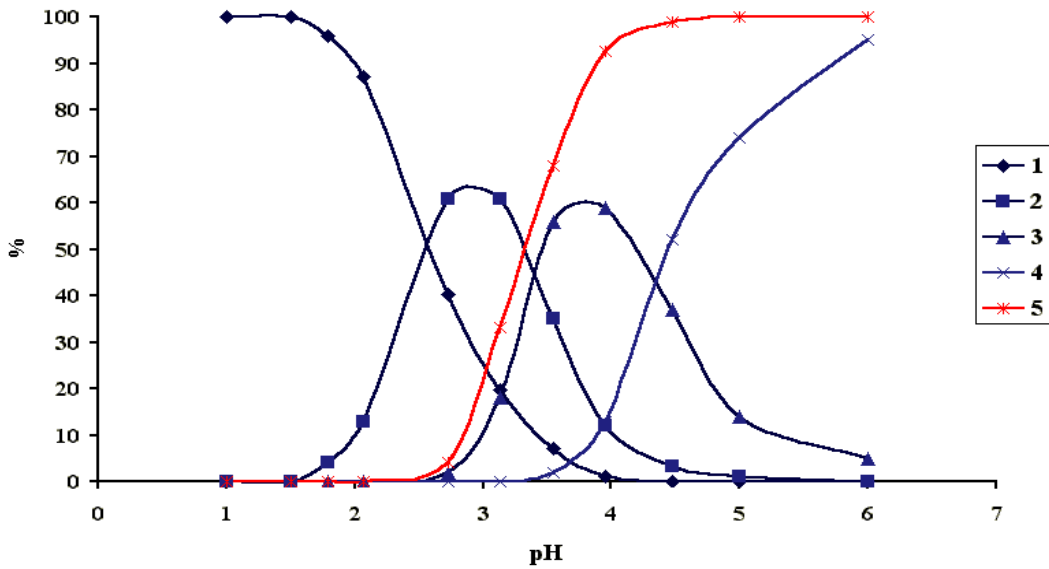


Fig.3. Speciation of Fe(III) in aqueous solution. 1 - Fe³⁺; 2 - Fe(OH)²⁺; 3 - Fe(OH)₂⁺; 4 - Fe(OH)₃⁰; 5 - pseudocolloids

concentrations, process such as the formation of pseudocolloids (sorption of radionuclides on the surface of colloidal impurities, that are always present in solution in micro quantities) may proceed in solution. For example, as seen from Fig.3, the second and consequent hydroxocomplexes, calculated using stepwise stability constants [4], are suppressed in the pH range in which the pseudocolloid formation proceeds in solution [1].

Hydrolysis of stable metals (Fe(III), Ni(II) etc.) that are often present in LRW at high concentrations can allow the system to proceed to the next step - formation of polynuclear hydroxocomplexes. The ability of polynuclear hydroxocomplexes and pseudocolloids to be retained by semipermeable membranes can then be used as a basis for their removal from solution by filtration through a proper membrane.

However, the presence of metal-complexing compounds complicates the radionuclide' behavior in solution. The complexing anion, ousting the OH- group from the coordination sphere of the metal-ion, may hinder formation of hydroxocomplexes and pseudocolloids in solution, or shift the onset of their formation to a higher pH range [5]. Mixed hydroxoacidocomplexes may also form in such solutions apart from hydroxo- and acidocomplexes.

The data presented above show that the speciation of radionuclides and stable metals in solution can strongly influence the effectiveness of radionuclide removal from LRW. The results show that, in order to optimize the removal of radionuclides from solution the following information is needed:

- The speciation of the radionuclides and stable metals in the aqueous solution. Specifically, how their state changes upon destruction of organic substances. This can be determined by applying a series of physico-chemical separation and analysis methods: centrifugation, ultrafiltration, dialysis, ion-exchange, spectrophotometry.
- The characteristics of sorption of the radionuclides on different absorbers as a function of radionuclide speciation in solution and nature of the absorber. Particular attention should be paid to the change in radionuclide hydroxocomplex sorption activity with the destruction of complexing agents and surfactants.

The effect of the following factors on the state and sorption behavior of the radionuclides in aqueous solution is to be investigated:

- pH;
- Presence and concentration of complexing anions in solution;
- Presence and concentration of stable metals in solution.

The data obtained as a result of the above proposed studies can provide a basis for development of effective methods for removal of radionuclides from solution and determine the maximum concentrations and forms of organic compounds that can be present without substantially reducing the effectiveness of the radionuclide removal process. A process that does not require complete destruction of all organic compounds will allow substantial reduction of energy related costs.

As a basis for development of an integrated process to destroy organic compounds in aqueous solution a novel method is proposed – a combination of ozonization and biochemical destruction - is proposed. Our preliminary experiments (Chlopin Radienvy Institute) showed that this combination has good potential.

The preliminary experiments for the combined ozonization and biochemical destruction process were carried out using a laboratory installation that consisted of the following: ozonization and biochemical reactors with thermoregulators, compressor, ozonizer, and process controlling devices (thermometer, pH-meter, air consumption meter). Oxygen chemical consumption was used to determine the total organic compound content in solution. The energy consumption required for destruction of the organic substances was calculated as a sum for solution heating, ozone formation, and transmission of air/air-ozone mixture to the solution. The results obtained show that energy consumption for destruction of a detergent can be significantly reduced by application of the proposed method (Fig.4).

However, additional experimental data are needed in order to develop a technology that could be used in practice. For every specific solution to be treated the following would need to be identified:

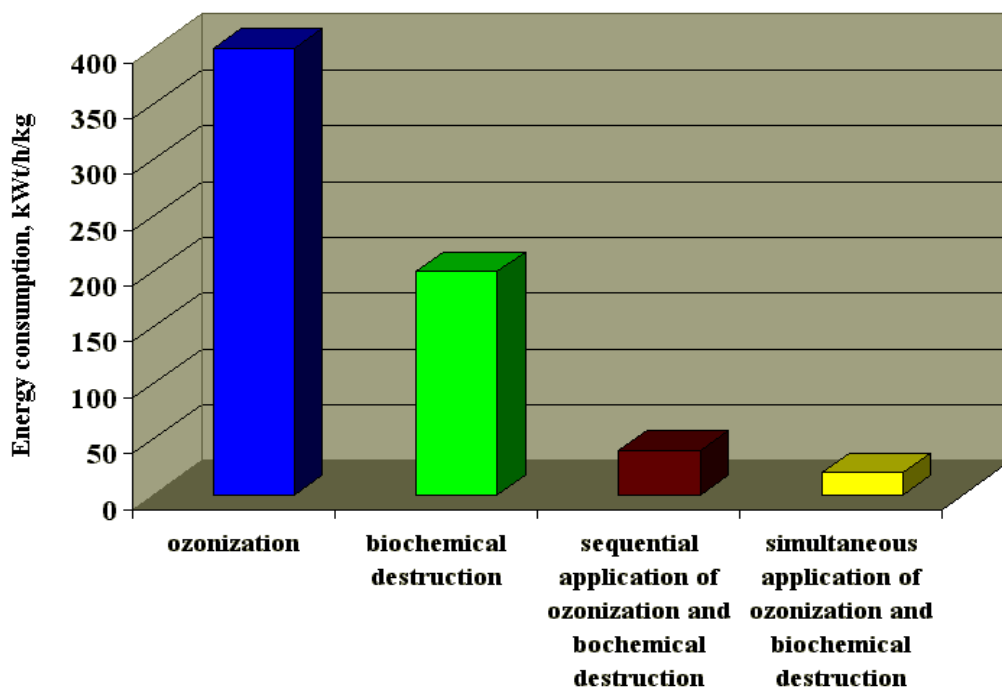


Fig.4. Destruction of $C_{12}H_{25}SO_4Na$ by different methods. Initial concentration - 200 mg/L; Concentration after treatment - 0.5 mg/L; $T=36^{\circ}C$; $pH=6.8$; air flow - 5L/L/Hour ; Ozone content in the ozone-air mixture -0.1-0.5 mg/L

- The optimal combination of ozone and biochemical destruction methods (simultaneous/sequential application of the methods)
- The optimal conditions (temperature, ozone concentration, destruction duration) for organic compounds destruction

To improve the efficiency and versatility of the multistep waste treatment method proposed, the following is suggested:

- Development of a method to convert organic compounds into passive forms that do not hinder the radionuclide removal processes

- Development of new improved methodologies for ozone and biochemical destruction of organic compounds, combining homogeneous/heterogeneous catalysis with a film regime for ozonization.

By devising improved methods for destruction of organic compounds in solution and studying how the state and sorption behavior of radionuclides changes with the destruction of organic compounds and pH changes in solution, we hope to develop an improved technology for treatment of mixed LRW. The preliminary data show that this method can have the following advantages:

- Low energy consumption for the destruction of organic substances and effective removal of radionuclides from solution
- Accomodation of solutions of various compositions with easy to make adjustments in process conditions
- Requirements for disposal of waste after treatment can be met.

An important potential application of the described methodology is to allow a wider range of more efficient surfactants and complexants to be used in decontamination procedures used in the maintenance and decommissioning of NPP. The proposed approach also is expected to be applicable in the development of technologies for cleaning up aqueous industrial waste containing heavy metals, various organic compounds, and oil.

References

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