

CLEANING OF LIQUID RADIOACTIVE WASTE BY THE METHODS OF OZONIZATION AND MAGNETIC SEPARATION

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ABSTRACT

The possibility for purification of liquid radioactive wastes (LRW) from organic compounds by the methods of ozonization and magnetic separation is studied. It is shown that addition of a finely divided ferromagnetic substance into LRW and subsequent filtration through a magnetic filter is an effective method for removal of emulsified organic compounds. The dissolved organic compounds are destroyed by ozonization. Some characteristics of the ozonization and magnetic separation processes are determined. The composition of the products of reactions between ozone and organic compounds is defined. The behavior of ^{137}Cs in the process of magnetic separation is investigated.

A feasibility of very good cleaning of LRW from emulsified organic compounds by means of successive application of the methods of magnetic separation and ozonization is confirmed.

INTRODUCTION

Organic impurities hinder cleaning of radioactive waste by evaporation, coagulation, ion exchange, and also impede using water from purified radionuclides in water recycling systems (1, 2).

We studied the feasibility of applying two known methods of cleansing using water systems for the processing of LRW: Ozonization and magnetic separation.

For cleaning emulsified organic compounds, we used the magnetic separation method's variant based on addition to the system under the processing of an auxiliary ferromagnetic substance (AFS), which are reusable particles. Ferromagnetic iron oxide powders were used as such a substance in this work. The diagram of the magnetic separation installation is presented in Fig. 1. The magnetic separator's filtering matrix was formed of steel balls 1-3 mm in diameter. The filtration rate was 100-150 m/h.

The organic compounds dissolved in the waste were destroyed by ozonization. Simultaneously, in the work, we studied the behavior of radionuclides which were encountered in the nuclear fuel wastes during the process of magnetic separation.

Magnetic Separation

Aqueous solutions simulating radioactive waste were prepared by adding main impurity components into distilled water. Emulsification of organic compounds was achieved by stirring. The ozonization parameters were the relationship of the vessel's and the stirrer's diameters, and the stirrer's rotation speed. These were chosen to provide an emulsion with a droplet size no more than 10 μm . Most attention among the radionuclides was paid to the behavior of ^{137}Cs which determines the NPP waste's radioactivity (3). The salt background in the model solutions was created by sodium nitrate and varied within the limits of 0.2 - 1.0 g/l, the pH being within the limits of 8 to 12.

In Figs. 2 and 3 there are presented microphotographs of preparations of turbine oil's initial emulsion and an emulsion which had undergone magnetic separation. The "forced breakthrough" technique enabled us to get an emulsion at the magnetic separator's outlet with the dispersed phase concentration sufficient for microscoping. The preparation was placed in a weak permanent magnetic field. Fast

flocculation was observed and the flocculi were formed at once as chains oriented along the lines of the force field. Such a behavior of the emulsion's nonmagnetic droplets was caused by the concentration of ferromagnetic iron oxide particles on their surface, as it similarly occurs in the known process of oil flotation. As a result, the emulsion droplets are additionally stabilized and acquire "quasi-ferromagnetic" properties. Based on these concepts, we put forward a method for quantitative evaluation of the optimal parameters of the process of magnetic separation of "oil-in-water" type emulsions, including evaluation of the relationship between the emulsions' dispersed phase and the AFS. It is based on the assumption that an effective separation of an emulsion is achieved when the mass of ferromagnetic substance floated by a single droplet becomes sufficient for separation of the droplet from the water flow by the magnetic field. These conditions are expressed quantitatively in the equation:

$$\psi \leq \min \psi \max \quad (\text{Eq. 1})$$

where $\psi \min$ is the minimum ratio between the masses of the organic and the ferromagnetic phases, sufficient to hold the flotation complex in the separator's magnetic field;

and where $\psi \max$ is the maximum phase ratio at which the flotation complex's stability in the magnetic field is preserved.

Considering the principal forces acting upon the flotation complex, in the separator's magnetic field, it is possible to evaluate quantitatively these relationships. The values of the interfacial tension and the wetting angle necessary for such an evaluation were determined experimentally, using, respectively, the anchor-ring method on torsion balance, and an original technique accomplished by pressing tablets of the AFS powder and directly measuring the wetting angle by means of a horizontal microscope with an angle meter. In Table I, the results of such measurements are presented. Based upon them, calculations are arrived at for two emulsion systems, using turbine oil in differing concentrations of detergent (Sulfonol NP-1, a sodium alkyl benzenesulfonate mixture). This data is compared with the results of experiments on magnetic separation in the same systems. As one can see, fulfillment of the relation (1) correlates with the high-efficiency of the separation, and vice versa.

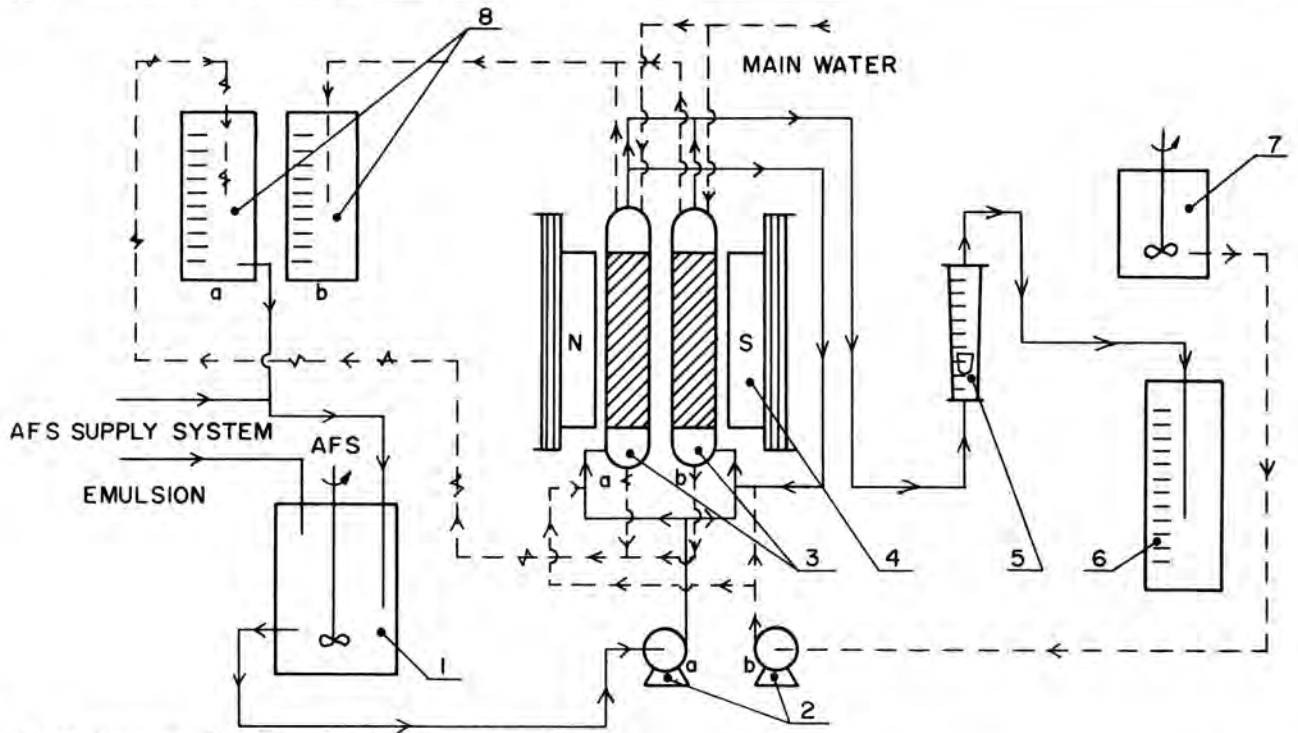


Fig. 1. Diagram of the Magnetic Separation System

1-tank for stirring emulsion with AFS; 2 (a,b)-pumps; 3 (a,b)-magnetic filters; 4-electromagnet; 5-rotameter; 6-collector of filtrate; 7-tank for preparing washing liquid; 8 9a,b)-collectors of washing liquid; filtration line; acid washing line; neutral

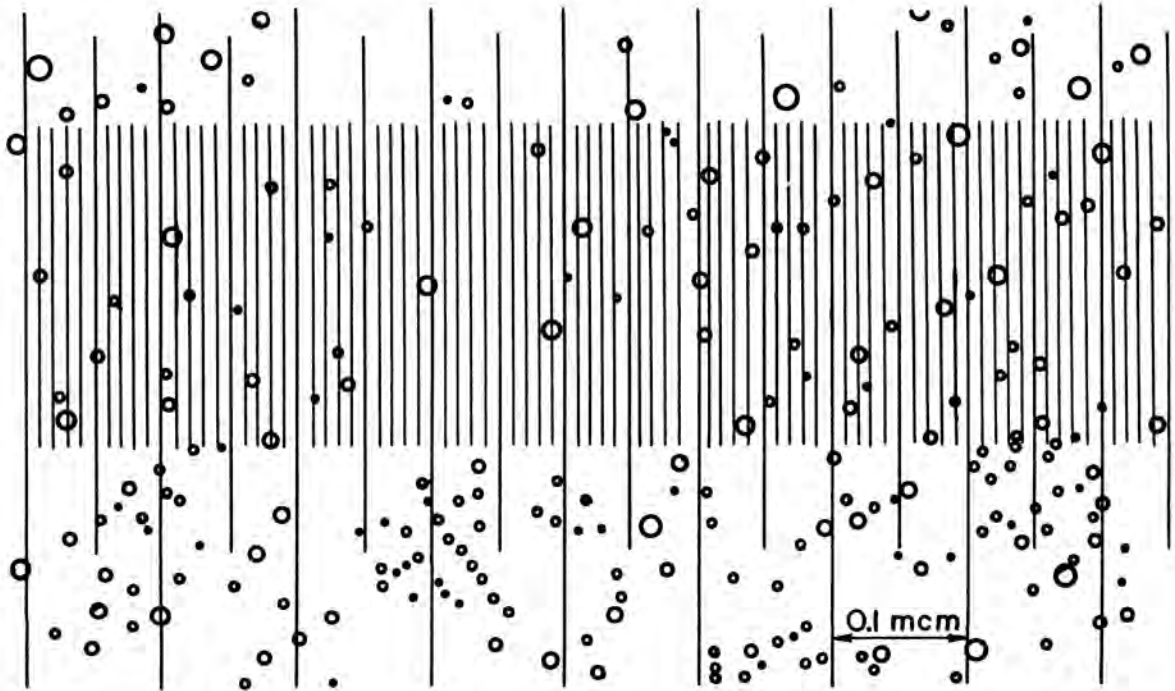


Fig. 2. Initial Emulsion.

Magnification x 90 (This is a redrawing of the photo-we did not have original photo.)

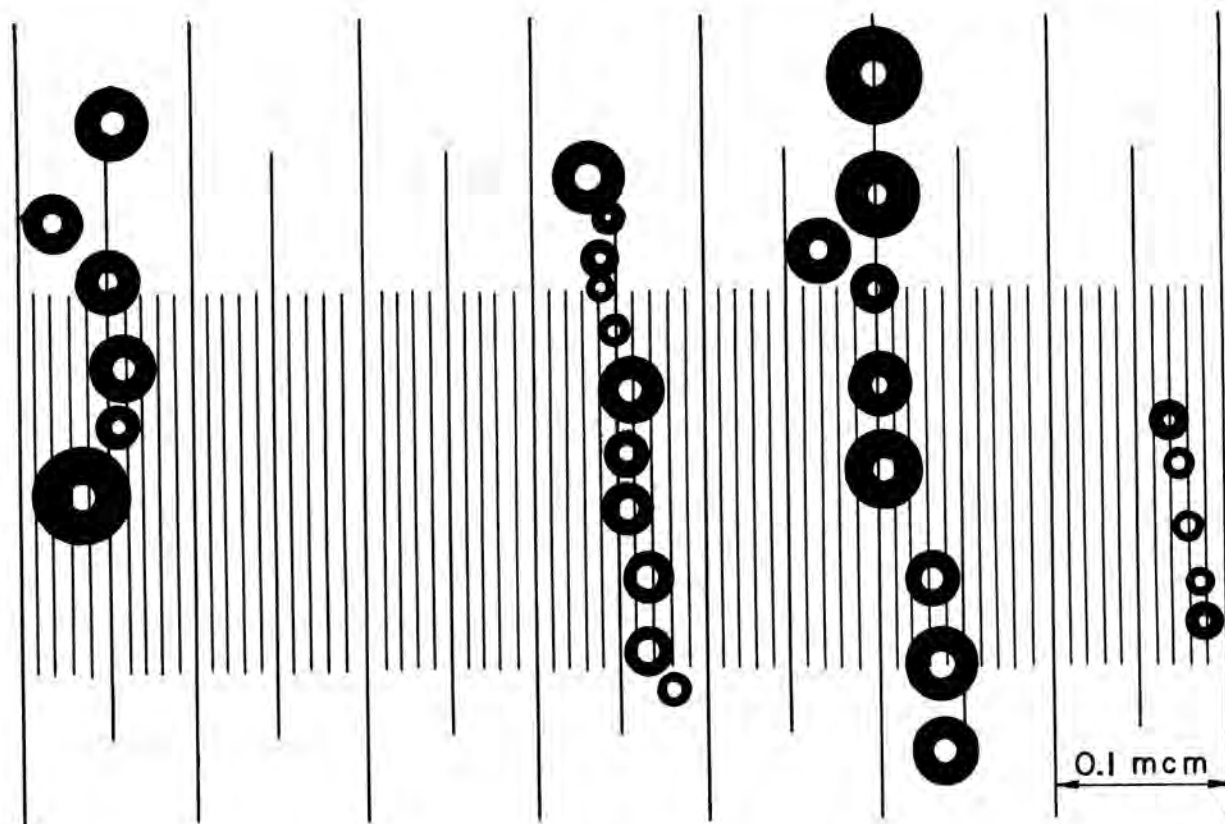


Fig. 3. Emulsion Having Undergone Magnetic Separation.
Magnification x 90 (This is a redrawing of the photo—we did not have original photos.)

TABLE I
Phase Ratios and Separation Efficiency of
Emulsion Systems

Temperature-20°C; oil concentration in emulsion-200 g/l;
AFS-power of magnetic hematite with particle size-1
mcm; confidence interval-0.95; min 0.1.

Detergent Concentra- tion, mg/1	Interfacial Tension, mN/m	Wetting Angle, Rad	Max	Separation Efficiency, %
0	18.6±0.9	0.51±0.04	0.24	95-99
100	12.0±1.0	0.16±0.05	0.05	50-60

The obtained results give grounds to the assumption that the considered variant of the emulsion magnetic separation process is based on the flotation interactions, and not on sorption interactions discussed in literature (4). The proposed approach enables an evaluation of priority concerning the efficiency of separation in different emulsions, depending on the physico-chemical and colloid-chemical properties. In particular, it was used as evidence for the feasibility of magnetic separation of the TBP emulsion, which was proven experimentally.

In studying the behavior of cesium-137, in the case of the emulsion magnetic separation (EMS), we established an essential increase of the AFS sorption activity in presence of an emulsified organic compounds, illustrated in Fig. 4.

The effect is observed irrespective of the organic phase's nature, as well as of the sorbent's nature, and seems to be connected with the flotation interaction between them.

Ozonization

Ozonization was performed by an ozone-air mixture barbotage through the solution. Residual concentrations of organic impurities were determined in samples taken of the solution, and in the concentrations of the non-reacted ozone in the off-gas from the reactor. Also, the influence of the pH and the temperature on the reaction rate was studied. The concentrations of the starting substances and the reaction products' composition were determined by using several independent methods of physico-chemical analysis: The gas and liquid chromatographies, the NMR and the mass spectroscopy.

It is established that the destruction of all of the compounds under study goes fastest in solutions with a pH which equals 8 to 10 at a temperature of about 60°C. The ozone consumption for their destruction varies mainly within the limits of 1-2 g/g of substance, the half-destruction time being from 0.5 to 30 minutes. Anions of organic and inorganic acids are formed as a result of ozonization. All of the products formed are less poisonous than the original compounds and inert in operations of LRW cleaning from radionuclides.

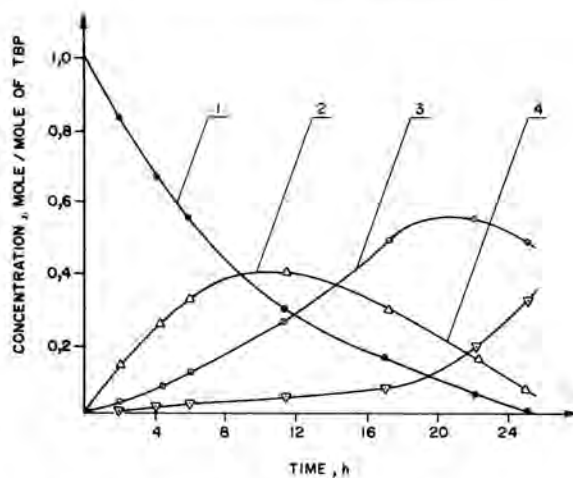


Fig. 4. Sorption of ^{137}Cs by the Auxiliary Ferromagnetic Substance. 1-at turbine oil concentration 200 mg/l, 2-in absence of oil, AFS-magnetic hematite powder.

Fig. 5. Accumulation of TBP Destruction Products in Ozonization of its Emulsion. 1-TBP, 2-dibutyl phosphoric acid, 3-monobutyl phosphoric acid, 4-ortho-phosphoric acid.

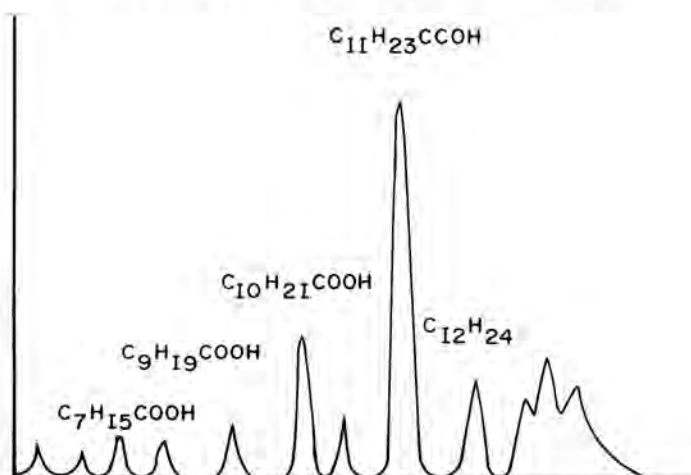


Fig. 6. Mass Spectrum of the Ozonization Products of Sodium Lauryl Sulfate.

TABLE II
Cleaning of NFC Aqueous Radioactive Waste by Magnetic Separation and Ozonization

Substance	Concentration, mg/l		After Ozonization	Destruction Products	Cleaning Factor	
	Initial	After Magnetic Separation			From Organic Impurities	From ^{137}Cs
Turbine Oil	200	1,0	0,2	Carboxylic Acids	$1/10^3$	200
TBP	800	300	0,1	PO_4^{3-} , Carboxylic Acids	$8 \cdot 10^4$	170
Hydrocarbon Diluent	300	0,5	0,1	Carboxylic Acids	$3/10^3$	150
Oxalate Ion	225		0,01	Water, CO_3^{2-}	$2 \cdot 10^4$	
Ethylenediaminetetraacetate	200		2	NO_3^- , CO_3^{2-}	$1/10^2$	
Detergents: Alkyl Sulfate	40		0,2	HSO_4^- , Carboxylic Acid	$2 \cdot 10^2$	
Alkyl Sulfonate	40		0,2	---"---	"	
Alkyl Benzenesulfonate	40		0,2	---"---	"	
Oxyethylated Alcohols	40		5	Carboxylic Acids	8	

through a magnetized matrix at a speed of 100 m/h. The specific consumption of the AFS was 0.5-1.0 g/g of organic impurity.

CONCLUSION

Thus, it follows from the presented data that the proposed technology provides good cleaning of aqueous radioactive wastes from different organic impurities. When an emulsified component is absent in the initial system, there is no need to use the non-destructive method of magnetic separation. The parameters of ozonolysis of the NFC organic reagents are essentially different. However, all these reagents have one common feature: The products of their destruction by the ozone do not have the technological and toxicological properties of the initial substances. This competitive technology is stipulated not only by its high efficiency, but also by its possibilities of reducing energy

consumption connected with the development of ozonizer equipment and the application of magnetizing systems on permanent and superconducting magnets.

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