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METHOD FOR EXTRACTING TRITIUM FROM TRITIUM-CONTAINING VACUUM-OIL WASTES

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The reactions resulting in the tritium contamination of mineral oils in pumps during transfer of tritium-containing gas mixtures are examined. The basic chemical forms of tritium dissolved in oils are established. The adsorption of tritium-containing impurities of spent oils and the chemical isotopic exchange of adsorbed impurities with concentrated sulfuric acid are studied. A method for handling tritium-containing waste oils that permits decreasing the radiation hazard due to storage of these oils and recycling tritium gas is proposed on the basis of these investigations.

One problem in the development of nuclear technology is salvaging organic radioactive wastes, which include spent mineral vacuum oils contaminated with tritium as a result of transfer of isotopic mixtures of hydrogen at enterprises and objects of nuclear technology. The content of tritium in oil used in diffusion and forevacuum pumps can reach 10^3 Ci/kg [1]. As a result of the high activity, such oil cannot be returned to the petroleum depot; it accumulates and is stored on the site of the works producing the wastes. In the last few years, a search has been conducted for a reliable and ecologically clean method for decontaminating tritium-containing oil wastes [2, 3].

Interaction of Tritium with Mineral Oils. Mineral oils used as working liquids in vacuum pumps are produced by deep purification of narrow fractions of low-sulfur petroleum. The number of classes of organic compounds comprising the main part of mineral oils is small: these are naphthene and aromatic hydrocarbons with side chains. The fraction of aromatic compounds is ordinarily small. Paraffins are also present in small quantities, and fresh oils contain no unsaturated hydrocarbons. However, the number of individual compounds in oils can reach several thousands [4].

We shall examine the basic chemical reactions occurring when the pumped tritium gas comes into contact with the hydrocarbons in oils. In the absence of oxygen, the dominant process is isotopic exchange by the Wilzbach free-radical mechanism, due to β decay of one of the nuclei in a tritium molecule followed by the exchange of a free tritium radical with an organic molecule [5]: $T_2 \to {}^3He + T$; $RH + T \to RT + H$ (R is a hydrocarbon radical). Tritium radicals can also form as a result of the interaction of β radiation from tritium with T_2 molecules: $T_2 \to T_2^* \to T + T$ (an asterisk denotes excited molecules). In addition, irradiation with β particles results in the formation of excited hydrocarbon molecules capable of reacting with dissolved tritium: $RH \to RH^*$; $RH^* + T_2 \to RT + HT$. Tritium is incorporated into hydrocarbon molecules a result of these reactions.

In the presence of oxygen, which enters the system unavoidably when pumps are operated, radiation-chemical oxidation of tritium ($T + O_2 \to OT + O$; $OT + T_2 \to T_2O + T$) and hydrocarbons ($RH^* \to R + H$; $R + O_2 \to RO_2$) occurs and

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peroxide radicals RO_2 are formed initially. The peroxide radicals react with hydrocarbons, forming hydroperoxides: $RO_2 + R'H \rightarrow ROOH + R'$. A characteristic feature of RO_2 radicals is their tendency to undergo isomerization, as a result of which intramolecular detachment of hydrogen occurs. An unpaired electron ($^\bullet$) is localized on a hydrocarbon chain, most often in the β position with respect to a —OOH group, which corresponds to the formation of a six-member transient state $R—CH_2—CH_2—C—O—O^\bullet \rightarrow R—CH^\bullet—CH_2—C—O—OH$ [6]. Such radicals are capable of interacting with tritium molecules forming selectively marked hydroperoxides: $R—CH'—CH_2—C—O—OH + T_2 \rightarrow R—CHT—CH_2—C—O—OH + T$. The hydroperoxides formed at the initial stage of oxidation are capable, in turn, of attaching hydrogen with formation and accumulation of new OOH groups (secondary peroxidation). The appearance of hydroperoxide groups at two neighboring carbon atoms involves breaking of C—C bonds and formation of ketones and carboxylic acids, including low-molecular acids. The attachment of a second peroxide group to naphthene hydrocarbons results in opening of the ring with formation of keto acids. The decomposition of hydroperoxides also occurs under exposure to tritium radiation. Here, the primary hydroperoxides decompose into aldehydes and water, the secondary hydroperoxides decompose into ketones and water, and the tertiary hydroperoxides decompose into ketones and alcohols.

The hydroperoxides formed with oxidation have a weak O—O bond and can generate radicals, decomposing in a monomolecular manner with breaking of this bond. In saturated and alkyl-aromatic hydrocarbons, hydroperoxides react with C—H bonds, likewise with formation of free radicals. The decomposition of hydroperoxides is catalyzed by alcohols, carbonyl compounds and carboxylic acids. Thus, in oxidizing oil, where diverse products of oxidation have formed and are present, the decomposition of hydroperoxides occurs in parallel according to several reactions. Consequently, the normal flow of the oxidation of oils at constant temperature is characterized by a *S*-shaped curve [4]. During the initial (induction) period of oxidation the properties of the oil do not change appreciably, This is followed by rapid accumulation of oxidation products, characterized by an increase of acidity. Subsequently, there is a period of retardation as a result of the formation of substances capable of inhibiting oxidation. At deep stages of oxidation, these are alcohols, acids, and water.

Many reactions of peroxide radicals and hydroperoxides with other particles result in the formation of stable products of oxidation: alcohols, carbonyl compounds, and carboxylic acids [6]. The isotopic exchange of tritium-containing moisture with alcohols and carboxylic acids ($ROH + T_2O \rightarrow ROT + HTO$) also results in the accumulation of tritium in oils, competing with the Wilzbach mechanism. As a result, tritium-containing alcohols, carboxylic acids, aldehydes, ketones, as well as water and products of condensation (including radiation-induced) of oxygen-containing compounds are present in spent oils [4].

When studying the interaction of tritium with organic molecules, it is necessary to take account of the fact that when one of the nuclei in a tritium molecule decays, initially, a molecular ion HeT^+ forms with probability 60% [7]. This ion is a strong acid (triton donor) and therefore is capable of isotopic exchange. According to the theory of isotopic exchange of hydrogen in organic compounds [8], tritium most easily replaces protium, which is found in a labile position, i.e., directly bound with hydrogen, and also nitrogen and sulfur. However, hydrogen which appears, for example, in aromatic nuclei or occupying the α position with respect to carbonyl, carboxyl, or other functional groups of oxycompounds is also capable of exchange [9, 10]. In this connection, the mechanism of introducing tritium into an organic compound by the method of gaseous exposure (Wilzbach method) exhibits appreciable selectivity, which has been repeatedly observed [9].

Determination of the Chemical Forms of Dissolved Tritium. According to the processes which have been studied in the spent vacuum-pump oils, tritium can be present in the following chemical forms: dissolved molecular tritium (T_2 or HT), tritium-containing hydrocarbons (RT), tritium-containing water (T_2O or HTO), and products of oxidation in which tritium can be bound with carbon and oxygen atoms. To choose the most efficient method for removing tritium from oils, it is first necessary to determine the fraction of each form. For this, preliminary experiments on extracting tritium from oil by means of bubbling, distillation, isotopic exchange, and adsorption were performed. The experiments were performed using a mixture which consisted of pure VM-5 vacuum oil with traces of tritium-containing spent VM-5 oil. The tritium content in the oil was analyzed on a SZhS-04k liquid scintillation β radiometer. A solution of *n*-terphenyl in toluene was used as the scintillator.

Bubbling gases through spent tritium-containing VM-5 vacuum oil gave the following results. Hydrogen bubbling does not lower the activity of the oil. Bubbling dry air decreases activity only by 8%. Preliminary saturation of air with water vapor increases this value to 16%.

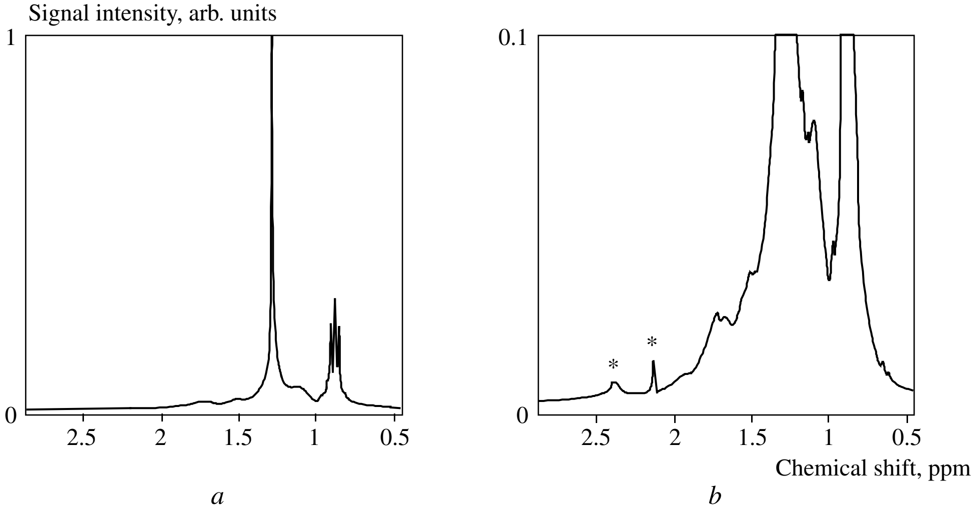

Fig. 1. Proton magnetic resonance spectrum of solutions of pure (*a*) and spent tritium-containing VM-5 oil (*b*) in deuterochloroform.

When solutions of spent oil in hydrocarbons of the kerosene fraction (boiling point 200–220°C) are distilled, the activity of the first fractions of the distillate is always appreciably higher than the activity of main quantity of the distilled substance. Nonetheless, most of the activity (more than 90%) is due to the bottoms. Thus, the tritium-containing components in spent oil have, primarily, low volatility. This precludes an appreciable presence of dissolved molecular tritium, tritium-containing light hydrocarbons, and water.

When oil is treated with water, water solutions of alkali and acids, and concentrated sulfuric and trichloroacetic acids the activity decreases appreciably: by 15–20, 30–50, and 80–90% in the case of water, water solutions of alkali and acids and concentrated H_2SO_4 and CCl_3COOH, respectively. In the case of sulfuric acid, the degree of tritium extraction increases with temperature. These results show that isotopic exchange reactions occur between tritium-containing components of oil and an inorganic phase. A large fraction of the tritium enters into slow isotopic exchange, of which the best catalysts are strong acids [8, 10]. The fraction of labile tritium (i.e., tritium which enters into rapid isotopic exchange with water in the absence of a catalyst) does not exceed 20%, but it can be underestimated because of the high stability of emulsions such as water in oil, which form components containing labile hydrogen. We also note that the increase in the degree of extraction when air is saturated with water vapor should be attributed to an isotopic exchange reaction.

The degree of extraction of tritium reaches its maximum value (95%) with adsorption purification of the oil with silica gel, alumogel, and zeolites. Thus, the main chemical forms of tritium in spent oils are heavy polar molecules, which can only be products of oxidation of hydrocarbons. About 5% of the tritium is not extracted with adsorption even after the purified oil is put into contact with fresh portions of adsorbent. This part of the tritium is probably bound with molecules which are identical to hydrocarbons in oil and are products of nonselective isotopic substitution.

The proton magnetic resonance spectra of solutions of pure and spent tritium-containing VM-5 oil in $CDCl_3$ are shown in Fig. 1. The chemical shift in parts per million (ppm) is determined relative to tetramethylsilane. The main peaks in both spectra correspond to methyl (the triplet 0.8–0.9 ppm) and methylene (singlet 1.25 ppm) of aliphatic chains. The small peaks in the range 2.1–2.4 ppm (marked by asterisks) are seen in the spectrum of spent oil. Signals due to hydroxyl of certain alcohols as well as aliphatic protons in the β position with respect to carbonyl, carboxyl, or ester groups are observed in this range. Thus, one can talk about the presence of alcohols, ketones, and (or) complex esters in spent VM-5 oil. The signals due to the carboxyl protons lie in the region which has not been investigated (9–12 ppm). Therefore, the presence of carboxylic acids in spent oil is also not ruled out. The absence of a water peak (near 5.8 ppm) is explained by its high, compared with the main components of the oils, volatility, so that it does not accumulate during pump operation.

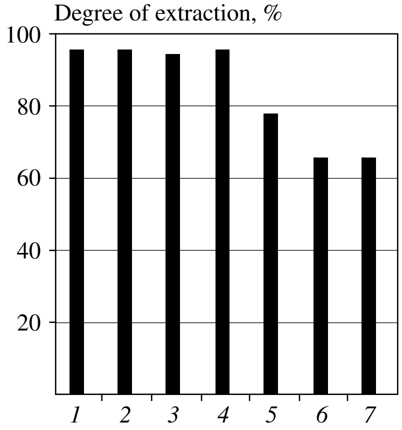

Fig. 2. Maximum degree of extraction of tritium by dry silica gel (*1*), alumogel (*2*), zeolites NaY (*3*), NaA (*4*), KA (*5*), moist silica gel (*6*), and activated carbon (*7*).

Adsorption of Tritium-Containing Impurities. Preliminary experiments showed that it is best to use adsorption concentration to extract tritium-containing impurities from spent oils. The completeness of detritization of oils was determined experimentally for many adsorbents. As one can see in Fig. 2, the deepest purification is achieved by using large-pore polar adsorbents: silica gel (95%), alumogel (95%), and zerolytes NaY (94%) and NaA (95%). When zeolite KA with approximately 0.3 nm entry openings is used, the degree of extraction decreases to 77%. On a nonpolar adsorbent (activated carbon), the degree of detritization is even lower: about 65%. The presence of moisture in the adsorbent decreases the degree of extraction. Thus, silica gel, on which a large amount of water is adsorbed (determined according to the color of the indicator silica gel), extracts tritium much worse.

The kinetics of the adsorption of tritium-containing molecules was studied in detail. The liquid phase, which was put into contact with the adsorbent, was mixed using a magnetic mixer with heating. In the course of the experiment, the temperature was maintained constant and the oil samples were periodically taken for analysis. In a series of preliminary experiments, a regime of mixing of the phases where the component of mass transfer due to diffusion in a liquid phase vanishes was chosen. Next, it was established that a change in the ratios of the amounts of the phases from 2 to 6 g of adsorbent for 20 ml of oil has no effect on the depth of purification, which attests to a substantial excess of adsorption centers over tritium-containing molecules. In this case, the adsorption must satisfy an equation of the first degree

$$\frac{N(t)}{N_0} = \frac{N_\infty}{N_0} + A\exp\left(-\frac{t}{\tau}\right), \tag{1}$$

where N_0 is the initial and N_∞ is the equilibrium number of tritium-containing molecules in the liquid phase (nonabsorbable residue); τ is the characteristic adsorption time, min; and, $A = (N_0 - N_\infty)/N_0$. However, analysis of the kinetic curves according to this equation led to success only for adsorption on activated carbon. For adsorption on polar adsorbents, the parameter τ does not remain constant during the process. Then, assuming, for example, two types of impurities, which are adsorbed from solution with different rates, are present in the liquid phase, Eq. (1) can be rewritten in the form

$$\frac{N(t)}{N_0} = \frac{N_\infty}{N_0} + A_1\exp\left(-\frac{t}{\tau_1}\right) + A_2\exp\left(-\frac{t}{\tau_2}\right), \tag{2}$$

where A_1 and A_2 are the fractions of the rapidly and slowly adsorbing impurities ($\tau_2 > \tau_1$). In this case, a least-squares fit of the kinetic curves obtained at 85°C on silica gel, alumogel, and zeolite NaY gives the parameters presented in Table 1.

TABLE 1. Parameters in Eq. (2) for the Adsorption Rate at 85°C

Parameter	Zeolite NaY	Alumogel	Silica gel	Activated carbon
N_∞/N_0	0.068 ± 0.008	0.028 ± 0.002	0.175 ± 0.007	0.31 ± 0.03
A_1	0.60 ± 0.06	0.62 ± 0.07	0.62 ± 0.03	0.66 ± 0.03
A_2	0.33 ± 0.06	0.36 ± 0.06	0.21 ± 0.02	–
τ_1, min	9.1 ± 3.8	9.0 ± 5.7	6.8 ± 0.9	115 ± 16
τ_2, min	101 ± 20	120 ± 39	66 ± 12	–

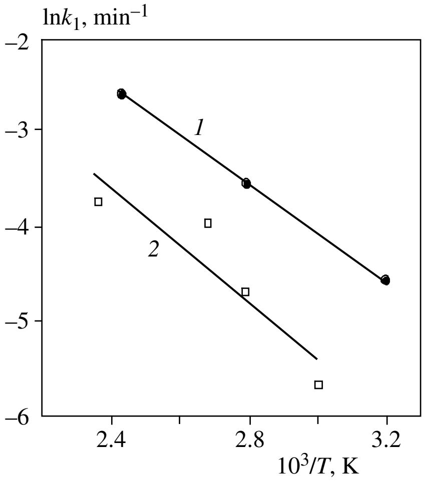

Fig. 3. Temperature dependence of the rate of adsorption of rapidly adsorbing impurities on zeolite NaY (*1*) and activated carbon (*2*).

As one can see from the data presented, the tritium-containing impurities are characterized by different adsorption rates which depend weakly on the type of adsorbent: the adsorption time is several minutes for impurities of the first type and 1–2 h for the second type. The fraction of impurities of the first and second types for polar adsorbents is almost the same. For adsorption on activated carbon Eq. (1) describes the kinetics of the process adequately: Eq. (2) does not improve the quality of the fit of the kinetic curves. We note that the observed biexponential character of the curves can also have a different interpretation, attesting, for example, to different adsorbed states of tritium-containing molecules.

Experiments on studying the influence of temperature on the adsorption rate show that at low temperature (up to 40°C) the rate constant ($k = 1/\tau$) is small and the adsorption equilibrium is established only over several days. Increasing the temperature substantially increases the rate constant. The section of the temperature dependence of the adsorption rate of rapidly adsorbing impurities $k_1(T)$ in the interval 40–150°C in Arrhenius equation coordinates

$$\ln k_1 = \ln A - E_a/RT$$

is a straight line (Fig. 3). The adsorption activation energy E_a is 22 kJ/mole for zeolite NaY and 25 kJ/mole for activated carbon. Such high values are probably due to the slow diffusion of large organic molecules in pores and channels in the adsorbent. To check this assumption, experiments on adsorption of tritium-containing impurities from oil, diluted with n-undecane, which should facilitate transfer of the adsorbate, on the zeolite NaY were performed. It was established that the dilution of oil by a nonviscous solvent does indeed increase the adsorption rate. Analysis of the results obtained using Eq. (2) gives the parameters presented in Table 2. It is evident that dilution decreases the characteristic adsorption times τ_1 and τ_2 severalfold.

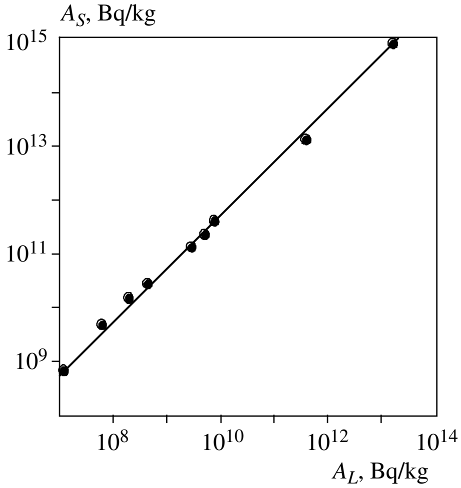

Fig. 4. Adsorption isotherm for tritium-containing impurities from spent VM-5 oil at 20°C.

TABLE 2. Parameters in Eq. (2) for the Rate of Adsorption by NaY Zeolite of Tritium-Containing Impurities from Oil Diluted with n-Undecane at 85°C

Parameter	Oil: n-undecane	
	1:1	1:3
N_∞/N_0	0.073 ± 0.009	0.079 ± 0.007
A_1	0.58 ± 0.07	0.50 ± 0.08
A_2	0.34 ± 0.06	0.42 ± 0.05
τ_1, min	3.5 ± 1.7	1.2 ± 0.4
τ_2, min	53.5 ± 10	15.4 ± 4.5

The adsorption equilibrium for tritium-containing impurities adsorbed from VM-5 oil on NaY zeolite at 20°C was studied in a wide range of equilibrium specific activity of the liquid phase: from $2 \cdot 10^{-4}$ to $2 \cdot 10^{2}$ Ci/kg. In this range, the adsorption isotherm follows a straight line well (Fig. 4). The total coefficient of adsorption of tritium

$$K = A_S/A_L,$$

where A_S and A_L are the equilibrium specific activities of the solid and liquid phases, respectively, is 64 ± 2. Additional experiments showed that the adsorption coefficient is slightly dependent on the temperature at which equilibrium is established (20–85°C), and depends much more strongly on the predrying temperature of zeolite, i.e., the amount of moisture in the zeolite.

Chemical Isotopic-Exchange Desorption. The high efficiency of the adsorption method for concentrating tritium-containing impurities makes it possible to use this method at the first stage of salvaging of spent oils for recycling tritium. Consequently, the next stage of the work was devoted to transferring the adsorbed tritium into a labile state. As already mentioned, a substantial fraction of the tritium in spent vacuum oils enters into isotopic exchange with concentrated sulfuric acid. In this connection, a decision was made to study the process of chemical-exchange desorption of tritium, i.e., desorption of tritium-containing impurities with simultaneously occurring chemical isotopic exchange.

TABLE 3. Dependence of the Degree of Tritium Extraction on the Desorption Conditions

Experiment No.	$V_{H_2SO_4}:V_{H_2O}$	T, °C	Desorption, h	Organic phase	Tritium content in the phase, %	
					inorganic	organic
1	9:1	85	2	n-Dodecane	90	0.1
2	9:1	20	5	n-Undecane	57	0.6
3	6:1	85	2	n-Dodecane	90	4.1
4	5:1	85	2	»	87	5.6
5	4:1	85	2	»	86	8.3
6	4:1	85	5	»	93	4.6
7	3:1	85	2	»	71	11
8	2:1	85	2	»	85	13
9	1:1	85	2	»	72	24

Tritium desorption from NaY zeolite was performed using water solutions of sulfuric acid with different concentrations. A weighed portion of the active adsorbent (1–2 g) was put into contact with a liquid phase (10–20 ml) with continuous mixing. In the course of the experiments with diluted sulfuric acid it was observed that the adsorbent granules are partially destroyed. When concentrated acid was used the color of the granules changed from light yellow to black. An oil film formed on the surface of the liquid phase. To determine the specific activity of the film, an organic solvent (n-undecane or n-dodecane) was added at the end of the experiment, after which the phases were mixed for another 30 min. Since the content of tritium in the organic and inorganic phases was determined in this part of the work, the solution of *n*-terphenyl in 1,4-dioxane was used for analysis. The conditions and results of the experiments are presented in Table 3.

The data presented show that the highest degree of extraction of tritium from the adsorbent (~90%) is achieved by using strong sulfuric acid: 60% and higher (experiments 1, 3) already after 2-h of desorption. As the acid is further diluted the degree of extraction, other conditions remaining the same, decreases (experiments 7–9). We note that the higher the acid concentration, the less tritium remains in the organic phase. The contact time between the phases also determines the degree of isotopic exchange between the desorbed tritium-containing molecules and the sulfuric acid (experiments 5, 6). Finally, as temperature is decreased, complete extraction of tritium from the adsorbent is not achieved even using a concentrated acid (experiment 2). This can be explained by the fact that high-concentration sulfuric acid gives rise to sulfonation, oxidation, and polymerization of the adsorbed organic molecules. Since the rate of isotopic exchange and the rate of reactions occurring in parallel depend differently on temperature, the degree of extraction can decrease sharply as a result of the accumulation of high-molecular products in the pores of the adsorbent and closing of further access of the acid.

Conclusions. The adsorption of tritium-containing products of oxidation and chemical-exchange desorption create grounds for developing a technology for returning tritium into production. Specifically, even at this stage of the investigations the following fundamental scheme for handling tritium-containing wastes of mineral vacuum oils can be proposed (Fig. 5). Spent oil with specific activity ~10^2 Ci/kg (then approximate tritium concentration in the flows is presented in the diagram), having completed the stage of adsorption purification, is subjected to oxidation. Catalytic oxidation with oxygen or one of the liquid-phase oxidation methods can be used for this [11, 12]. The low-activity tritium-containing waste waters formed are condensed, bound in cement, and buried in the form of cement blocks. The adsorbed tritium-containing impurities are transferred into a liquid phase by chemical isotopic-exchange desorption. When the desorption is complete the tritium concentration in the liquid phase increases by a factor of 10, after which the sulfuric acid is neutralized, the water formed is decomposed on metal, for example, magnesium at high temperature, and hydrogen, containing a substantial quantity of tritium, can be reversibly sorbed by hydride-forming metals (U, Ti) or alloys, stored and used when needed. The oxides formed at the water decomposition stage are used to neutralize the acids, which decreases the consumption of reagents and the quantity of solid wastes. The spent adsorbent, sulfates, and other solid substances are also bound in cement blocks.

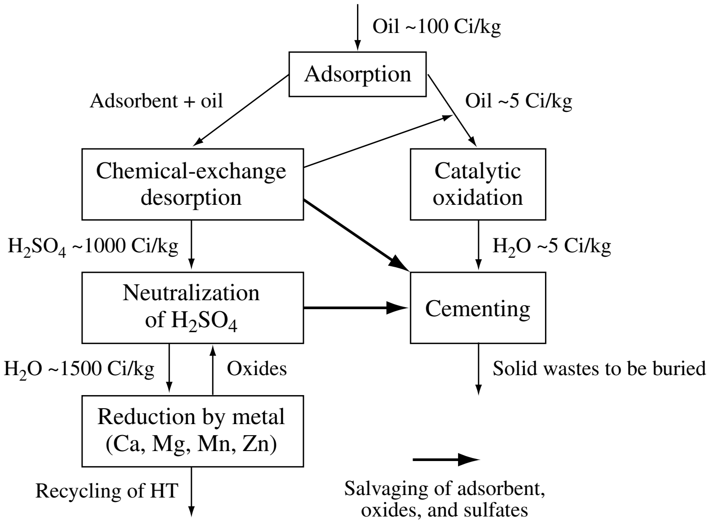

Fig. 5. Schematic diagram showing the handling of tritium-containing mineral-oil wastes using adsorption concentration of tritium.

This method of handling substantially decreases the radiation hazard due to the storage of oil wastes with high specific activity. The aggregate state and chemical composition of most of the oils remains unchanged during the tritium extraction process. The additional wastes formed are solid wastes, and their volume is negligible compared with the volume of the oil wastes.

REFERENCES

1. L. F. Belovodskii and V. K. Gaevoi, "Tritium contamination of structural materials," in: *Interaction of Hydrogen Isotopes with Structural Materials* IHISM-01, International seminar, Sarov, VNIIÉF (2002), pp. 294–303.
2. K. Klasson, P. Taylor, R. Cummins, and B. Evans, *Removal of Mercury and Tritium from DOE Waste Oils*, ORNL/TM-13751 (1999).
3. *Nochar Petrobond Absorbent Polymer Tritiated Oil Solidification*, Report of Nichar Inc. for the US Department of Energy 2313 (2001).
4. N. I. Chenozhukov, S. É. Krein, and B. V. Losikov, *Chemistry of Mineral Oils*, Nauka, Moscow (1959).
5. E. Evans, *Tritium and Its Compounds* [Russian translation], Atomizdat, Moscow (1965).
6. N. M. Émanuél', E. T. Denisov, and Z. K. Maizus, *Chain Reactions of Oxidation of Hydrocarbons in the Liquid Phase*, Nauka, Moscow (1965).
7. P. Souers, *Hydrogen Properties for Fusion Energy*, University of California Berkeley Press (1986).
8. A. I. Brodskii, *Chemistry of Isotopes*, Izd. Akad. Nauk SSSR, Moscow (1952).
9. G. G. Gusev and Yu. M. Kapustin, *Tritium in Organic Chemistry*, Atomizdat, Moscow (1966).
10. G. P. Miklukhin, *Isotopes in Organic Chemistry*, Izd. Akad. Nauk Ukr. SSR, Kiev (1961).
11. *Direct Chemical Oxidation*, Report of the Lawrence Livermore National Laboratory for the US Department of Energy 109 (1998).
12. *Acid Digestion of Organic Waste*, Report of the Savannah River Technology Center for US Department of Energy 1827 (1999).