FRACTIONATION OF LIQUID HIGHLY-RADIOACTIVE WASTES AND INCORPORATION OF LONG-LIVED RADIONUCLIDES INTO CERAMICS AND VITREOUS COMPOSITIONS

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ABSTRACT

The combination of the HLW fractionation flowsheet with a subsequent incorporation of concentrates into vitreous-like or ceramic compositions enables us to use some radionuclides and to more efficiently realize a concept of final waste disposal.

The investigations of the properties of extractants based on carborene complexes resulted in the development of a technological flowsheet for cesium and strontium recovery. Along with these works, investigations of the extraction of trivalent elements were conducted.

The conditions were elaborated for incorporation of simulated concentrates of long-lived radionuclides into vitreous and ceramic compositions which could be considered as forms for final disposal.

Overcoming the problem of management of high-level liquid radioactive wastes (HLW) arising from the reprocessing of spent nuclear fuel is one of the most significant requirements for the development of nuclear power. The need for reprocessing of HLW is caused by the long-term safe storage of this waste and by the demand for some radionuclides for commercial use.

The storage of solidified HLW in the form of glass or other chemical resistant compositions provides safe isolation from the biosphere. The volume of solidified waste depends on the chemical additives and corrosive products rather than on radionuclide content. So, the separation of long-lived radionuclides, such as ^{90}Sr, ^{137}Cs, TPE (^{241}Am, ^{243}Am, ^{244}Cm) and RE (^{144}Ce, ^{144}Pr, ^{147}Pm), enables us to considerably reduce the volume of waste for long-term storage.

Specialists from different countries paid much attention to this problem, but up to now, no suitable method was proposed which could afford complete recovery of these elements. The efficient separation of them is of great importance for such technology.

Therefore, particular emphasis is placed on the development of a simple extraction flowsheet for HLW processing which has considerable advantages over the flowsheets based on alternative processes.

Great progress towards the solution of this problem was made by Soviet and Czechoslovak investigators. They proposed an extraction system using polyhedral carborene complex in a mixture with polar diluent and polyethylene glycol.

The extraction properties of carborene complex were investigated with respect to cesium, strontium and accompanying impurities. Also, chemical and radiation resistance of the extraction system, corrosion aggressivity, solubility of extractant in aqueous phase, to explosion and fire danger of the process were studied.

Extensive studies of the properties of the extractants based on the carborene complex led to the development of a technological flowsheet for the recovery of cesium and strontium from HLW and to tests with highly-active raffinate of spent WWER fuel reprocessing (1).Strontium and cesium were directly extracted from acidic solutions without any preliminary adjustment. From the volume of several tens m3 HLW 300 kCi of ^{90}Sr and the same quantity of ^{137}Cs were recovered (2). Test data have shown that the recovery of cesium and strontium exceeds 99%. The decontamination of strontium from cesium is over 10^3 and that of strontium and cesium from accompanying elements is 5 o 10^2, respectively. The extractant proves to be of a high radiation and chemical stability and can be recycled.

Along with the development of the Cs and Sr recovery process, the investigations on the extraction of trivalent elements were conducted. It is of interest to note that the extraction system with the carborene complex proved to be useful for the recovery of transplutonium elements and rare earths (3).

The investigations performed result in the development of a combined flowsheet which permits, by means of different technological procedures, almost complete recovery of cesium and strontium radionuclides, rare earths and transplutonium elements, being directed into individual streams. The principal flowsheet is presented in Fig. 1.

Bench tests have shown that under experimental conditions, the concentrations of cesium were sixfold, strontium tenfold, and TPE two to threefold. Rather high separation coefficients of extracted elements were attained in this case as well.

The obtained concentrates can be directed for immobilization in the form of glass or ceramic compositions.

The combination of the flowsheet for HLW fractionation with subsequent incorporation of long-lived radionuclides into ceramics or vitreous compositions allows for development of a more versatile and reasonable concept for final disposal of wastes. Besides, this combination makes it possible to decrease the size of solidification facilities, to increase reliability for immobilizing the radionuclides in a solid matrix and to use them as ionizing radiation sources.

Bench equipment "Grom-1" (4) was designed and manufactured for the solidification of ^{137}Cs and ^{90}Sr

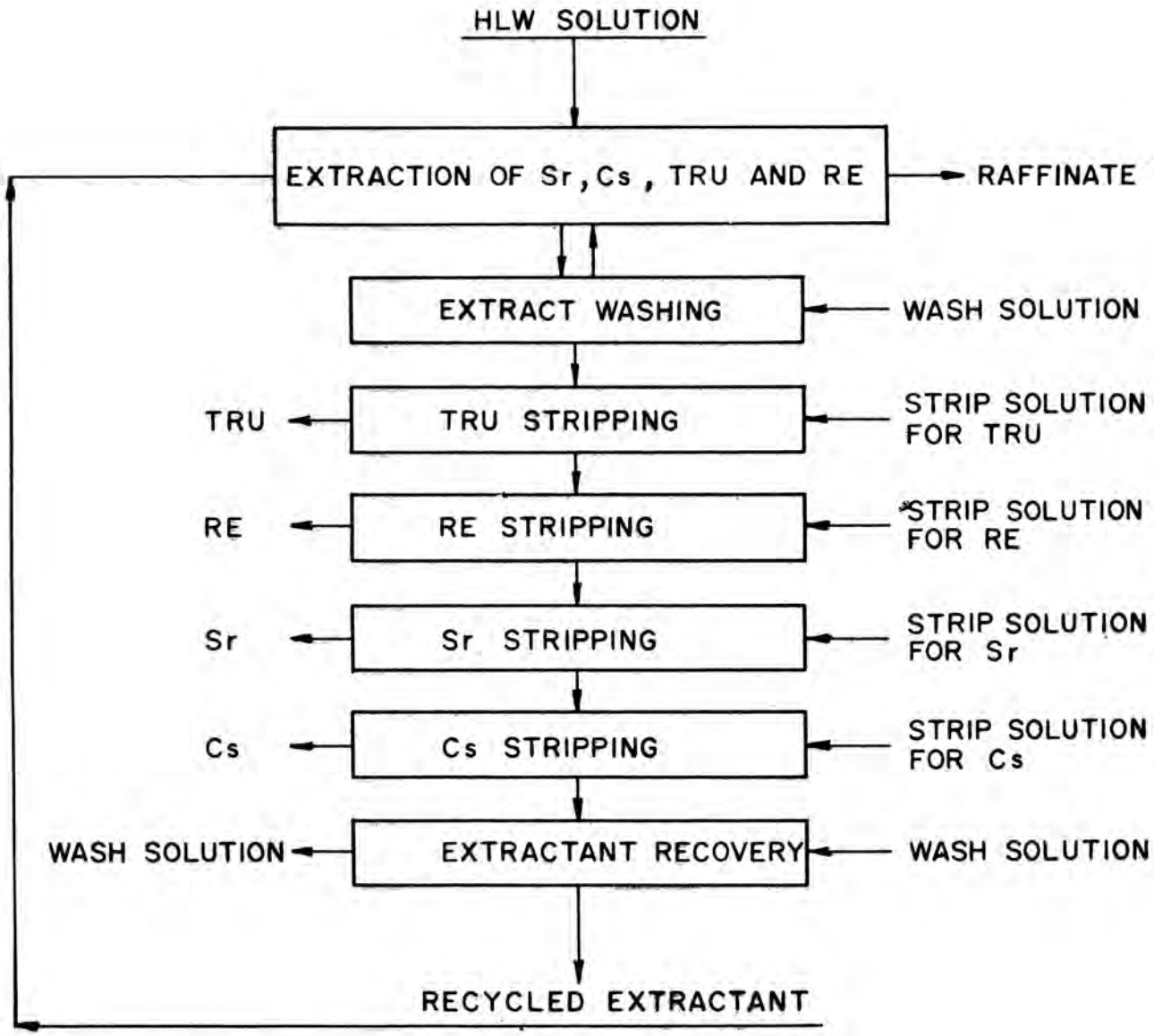
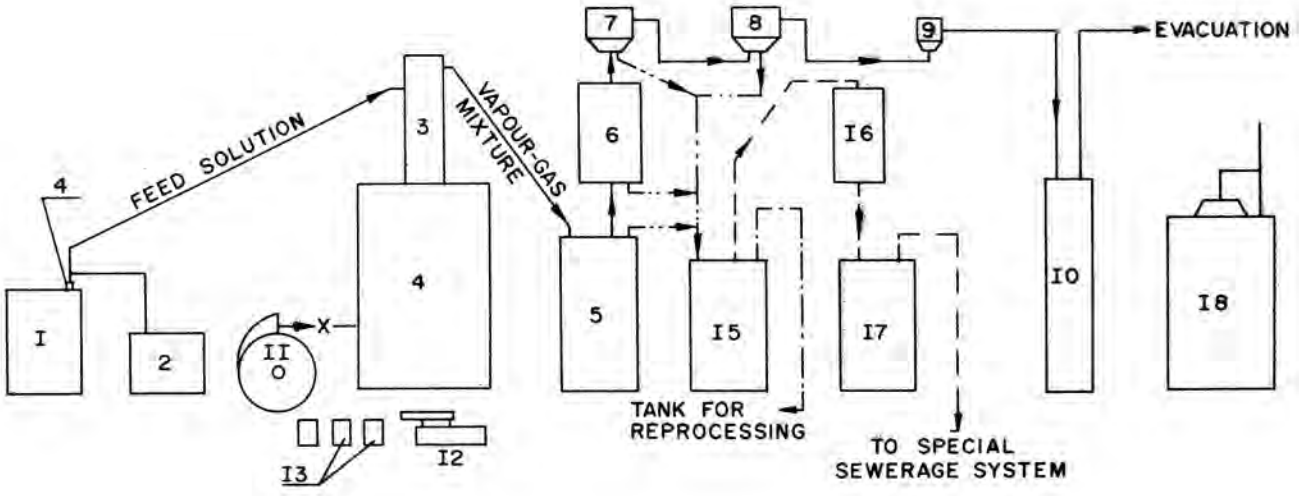


Fig. 1. Principal Extraction Flowsheet for HLW Combined Reprocessing.



1 - Tank with solution to be reprocessed;
2 - Dose pump;
3 - Thin-film evaporator;
4 - Melting furnace;
5 - Condenser;
6 - Cooler;
7, 8, 9 - Filters;
10 - Neutrolizer;
11 - Air injector;
12 - Receipt disc;
13 - Containers for glass mass;
14 - Dose valve;
15 - Evaporator;
16 - Condenser;
17 - Collector for condensate;
18 - Furnace for vitromet produc

Fig. 2. Diagram of Grom-1 Equipment.

concentrates in the form of glass blocks or vitreous compositions.

Figure 2 presents a basic diagram of the facility comprising the following main units:

- Preparation of the feed solution,
- Denitration and evaporation,
- Glass-melting and granulation,
- Receipt and formation of glass granules,
- Inclusion of glass granules into metallic matrices, and
- Vapor purification systems.

The facility is installed in two standard hot cells. Throughput is 5 dm^3 of flux solution per hour. Thermal denitration and evaporation of the solution is carried out in a film-rotary evaporator with steam-heating. Complete dehydration, calcination and glass boiling are performed at 1,000-1,100°C in a ceramic pot in the resistance furnace. In the bottom part of the pot, there is a melt-discharge pipe.

Vapor mixture is delivered through the water cooler to the condenser. Then, the vapor flow passes in succession to other installations within the gas purification system including cooler, filters, column for NO_x entrainment and absorption column.

The efficiency of this gas purification system was tested on the reprocessing of simulated cesium concentrates which could have arisen from HLW fractionation. It was found that the main quantity of entrained cesium is captured in the condenser. Overall entrainment in the experiments did not exceed 0.2-0.6% of the total cesium amount in the solution.

The facility also contains a unit for the evaporation of secondary liquid wastes from the condenser and the filters. After evaporation, the concentrate is again transferred to vitrification.

The design of the resistance furnace enables a remote replacement of heaters and the melter crucible at regular intervals.

For the vitrification of ^{137}Cs concentrates, alumophosphate glass was prepared which can contain up to 30-50% of the cesium oxide. Density of this glass is 2.8-3.3 g/cm^3, with specific activity of 40-55 Ci/cm^3. Equilibrium values of ^{137}Cs as per leaching rate in distilled water lie in the range of $2.5 \cdot 10^{-7}$-6, $5 \cdot 10^{-6}$ $g/cm^2 \cdot d$.

The conducted investigations have revealed that the glass structure is formed on the basis of fragments of pollucite-like compounds and this is responsible for low leaching rates (5).

Borosilicate glass provides a better matrix for vitrification of ^{90}Sr concentrates. In this case, glass can incorporate over 50% of the strontium oxide and exhibits strong leaching-out resistance. The density of glass is 3.5-3.7 g/cm^3. Due to high specific activity, this glass may be used as ionizing and heat radiation sources.

In order to generate an additional barrier preventing penetration of radionuclides into the environment, a process for the inclusion of glass granules into the metallic matrices has evolved.

Vitreous compositions were prepared by pouring the intergranular voids into a perforated container, pressing the latter into molten metal, then executing a vacuum-suction of the melt. As metals, the commercial zinc, aluminum alloys and technical lead were used.

Some data on the properties of glass granules and vitreous compositions are given in Table 1.

TABLE I

Properties of Glass Granules and Vitromet Compositions Produced in Grom-1

GLASS GRANULES	
Diameter	5.0 6.5 mm
Impact strength	4.1 21.8 MPa
Microhardness	3.5 4.0 GPa
Wear (in mass %)	$(1.5\ 4.0) \cdot 10^{-2}$
Leachingrate	106 107 $b/(cm^2 \cdot d)$
VITROMET COMPOSITIONS	
Water absorption	0.1 0.25 %
Volume porosity	1.0 3.0 %
Leachingrate	107 108 g/(cm2 d)
Diffusion coefficients ($m^2 \cdot s^{-1}$)	
^{90}Sr (Al)	$(1.6\ 9.5)\ 10^{-17}$ (450 - 620 °C)
^{90}Sr (Zn)	5 1015 (377°C)
^{134}Cs(Al)	21016 (600°C)
^{134}Cs(Zn)	51015 (377°C)

A two-stage process for the solidification of TRU wastes with ceramic compositions based on natural clays is worked out. In the first stage, the concentrate calcination is performed in a sloped, rotary-tube type furnace with three-zone resistance heating. Variations in calcination conditions are achieved by the choice of zone temperature, change in tube rotation speed and in the feed rate of TRU wastes. Under the optimum operating conditions, the apparatus assures the production of finely-dispersed calcine with a high annealing degree of organic compounds and with a low content of residual nitrogen. Elimination of adhering accumulations of calcine on the inner surface of the rotary tube and a decrease of its dust-entrainment with a steam-gas flow are attained by means of some specific additions affecting the calcination conditions *to a great extent*.The second stage of the process involves the manufacture of ceramics from the mixtures of calcine and natural clay in commercial equipment commonly used in the ceramic industry. For better drying and annealing, ceramic specimens are made in the form of cylinders 10-12 mm in diameter and thickness. Drying and annealing are carried out in resistance furnaces under conditions providing complete sintering of the ceramic crock (water absorption is no higher than 2%). The

optimization of operating conditions as applied to different compositions of charges, in terms of waste content and corrective additions, is achieved by changing the final temperature and/or annealing time. The process under development admits combined incorporation of different wastes into ceramic compositions: For example, simultaneous incorporation of TPE concentrates and perlyte pulp. The waste content in obtained ceramics may come to 30-40% as a function of composition.

The chemical stability of ceramics is found to be quite high as for borosilicate glass. Values of water tightness determined in Soxlet apparatus, for the specimens obtained, are within the limits of $(4 + 9) \cdot 10^{-4}$ g $\cdot cm^{-2} \cdot d^{-1}$. Leaching rates of ^{137}Cs and ^{241}Am in deionized water at 25° C are $(2 + 7) \cdot 10^{-6}$ and $(1.5 + 5.5) \cdot 10\text{-}8$ g$\cdot$ $cm^{-2} \cdot d^{-1}$ respectively. The limiting value for compressive strength is not lower than 35 MPa.

The consideration of total properties of vitreous and ceramic compositions, as well as production technology in facilities with throughput of 5-10 l/h, allows us to draw conclusions about the promising combination of the HLW fractionation flowsheet with the solidification of small amounts of concentrates of long-lived radionuclides.

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