THERMOCHEMICAL PROCESSING OF RADIOACTIVE WASTE USING POWDER METAL FUELS

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Abstract

Problematic radioactive wastes were generated during various activities of both industrial facilities and research institutions usually in relative small amounts. These can be spent ion exchange resins, inorganic absorbents, wastes from research nuclear reactors, irradiated graphite, mixed, organic or chlorine-containing radioactive waste, contaminated soils, un-burnable heavily surface-contaminated materials, etc. Conventional treatment methods encounter serious problems concerning processing efficiency of such waste, e.g. complete destruction of organic molecules and avoiding of possible emissions of radionuclides, heavy metals and chemically hazardous species. Some contaminations cannot be removed from surface using common decontamination methods. Conditioning of ash residues obtained after treatment of solid radioactive waste including ashes received from treating problematic wastes also is a complicated task. Moreover due to relative small volume of specific type radioactive waste the development of target treatment procedures and facilities to conduct technological processes and their deployment could be economically un-expedient and ecologically no justified.

Thermochemical processing technologies are used for treating and conditioning problematic radioactive wastes. The thermochemical processing uses powdered metal fuels (PMF) that are specifically formulated for the waste composition and react chemically with the waste components. The composition of the PMF is designed in such a way as to minimize the release of hazardous components and radionuclides in the off gas and to confine the contaminants in the ash residue. The thermochemical procedures allow decomposition of organic matter and capturing hazardous radionuclides and chemical species simultaneously. A significant advantage of thermochemical processing is its autonomy.

Thermochemical treatment technologies use the energy of exothermic reactions in the mixture of radioactive or hazardous waste with PMF. When used energy of exothermic reactions in waste thermochemical treatment processing, the problems concerned with heating method choice, appropriate heating equipment operation, and maintenance of this equipment reliability are excluded. Generally, the PMF consists of combustible powder metal, oxygen-containing component, and some additives (pore-forming materials, stabilizers, surface-active substances, and other) with a predominance of metal powder. A thermodynamic simulation is applied widely at the designing of the PMF.

Introduction

Moscow Scientific and Industrial Association "Radon" has been developing intensively radioactive waste thermochemical treatment technologies for pre-treatment (e.g.

decontamination), treatment and conditioning of specific types of radioactive wastes: spent ion exchange resins, inorganic absorbents, wastes from research nuclear reactors, irradiated graphite and zirconium, mixed, organic or chlorine-containing radioactive waste, contaminated soils, un-burnable heavily surface-contaminated materials, etc. Thermochemical treatment technologies use the energy of exothermic reactions in the mixture of radioactive or hazardous waste with special powder metal fuels (PMF). When used energy of exothermic reactions the problems concerned with heating method choice, appropriate heating equipment operation, and maintenance of this equipment are excluded.

The composition of the PMF is designed in such a way as to minimize the release of hazardous substances and radionuclides in the off gas and to confine the contaminants in the mineral or glass-like end products. Generally, the PMF consists of combustible powder metal, oxygen-containing component, and some additives (pore-forming materials, stabilizers, surface-active substances, and other) with a predominance of metal powder. Thermodynamic simulation is applied widely at the designing of the PMF followed by experimental performance and operational safety assessment tests[1].

Currently, the thermochemical treatment technologies were developed and demonstrated to be feasible as follows:

A. Thermochemical decontamination of metals, asphalt, and concrete.
B. Processing of spent ion exchange resins, plastics, polymers, medical waste, biological objects.
C. Autonomous vitrification of ash residues, calcinates, spent inorganic sorbents, contaminated soils, and the like.
D. Processing of carbon with ^{14}C retention: reactor graphite, lubricants, moulds, etc.
E. Processing of fuel rod zirconium by chemical including into mineral-like materials.

Thermochemical decontamination

The decontamination technique based on application of PMF is used in order to decontaminate a surface of asphalt, concrete, metal. This can be expedient when the radioactive contamination is strongly fixed in the near surface layers of material and conventional decontamination methods cannot remove radionuclides[2]. The thermochemical decontamination process is based on thermal treatment of superficial layer of contaminated material by the heat generated due to combustion of a layer of PMF covering the surface. The PMF layer on the surface is burning continuously and flameless within a few - a few tens on minutes. Due to heating the radionuclides are most volatilized being thereafter trapped by the slag layer, which is produced as a result of PMF combustion. Thermochemical interaction between the slag layer and material can result also in a removal of a near surface layer along with contaminating radionuclides.

The thermochemical decontamination technology is rather simple and comprises few operations[3]. First operation is determining the contamination spot configuration followed by covering of contaminated spot of the surface with a thin (0.8 – 1 cm) layer of PMF. This layer is then ignited combustion lasting for a few – a few tens of minutes depending on the PMF type. The last stage of decontamination technology follows after burn out of PMF, representing collection of obtained slags for safe transportation. The decontamination efficiency depends mainly on temperature and duration of a surface heating. These are determined by PMF formula and PMF consumption per unit of the treated area. The process optimization for various materials includes selecting the mixture composition, ensuring necessary combustion temperature, by using thermodynamic calculation, and the heating duration. The composition and amount of slags formed at PMF combustion and determined both experimentally and calculated thermodynamically are also the matter of concern.

Decontamination of the metal surface is achieved as a result of radionuclides volatilization and fixation in a slag layer that forms at PMF combustion. For the removal of strongly fixed radioactive contaminations from a metal surface, as a rule, the removal of a thin material superficial layer is necessary. Eventually relative deep penetration of radioactive contaminants into metals occurs, which can be caused by corrosive and mechanical destruction of near surface metal structure. A special thermochemical technique has been developed for deep decontamination of metals, which combines of both thermal volatilization and chemical surface oxidation of metal. It allows decontamination of metals at depths as 100μ[4].

Thermochemical decontamination of concrete is mostly based on the effect of concrete spallation caused by PMF combustion thermal shock. The PMF filling layer is coated on the contaminated concrete plate and ignited. At the completion of PMF combustion process, the concrete upper layers crack and spall. These concrete fragments spalled together with slags are removed after slag cooling down. The decontamination efficiency for concrete reaches 90-95% per one decontamination act. The depth of removing radioactive contamination is up to 5 –8 mm. Decontamination procedures can be repeated if necessary. For example at greater depths of contamination one can achieve necessary clean up by removal a few layers of contaminated concrete.

For the decontamination of asphalt the transfer of the contaminated layer to the softened state of asphalt is achieved occurring at temperatures 130 – 180°C. As in the case of metal surface, the PMF filling with a glass-fiber backing is coated on the contaminated spot of asphalt surface. The softened asphalt afterward is easily removed mechanically on a depth necessary for complete cleaning. The deeper is the radionuclide contamination of asphalt the longer shall last the PMF combustion and consequently the thicker shall be the PMF layer. The main characteristics of thermochemical decontamination method are given in Table I.

Table I. The characteristics of thermochemical decontamination process.

Material	Maximal achieved temperature (°C)	Duration of process (min)	Efficiency of decontamination (%)	Radionuclides carry over (^{137}Cs) (%)
Metal	1100	20	95 - 99	0.1 – 0.5
Asphalt	400	15	99.9	0.1 – 0.5
Concrete	1300	20	95 – 99	0.1 – 0.5

Processing of spent ion-exchange resins

Some organic radioactive wastes require special treatment technologies. These can be spent ion exchange resins (IER), mixed, polymer, and chlorine-containing (for example PVC) wastes, biological objects, etc. The thermochemical processing of radioactive organic waste is based on application of specifically formulated PMFs. The composition of these PMFs is designed by using thermodynamic calculations taking into account chemical composition of waste. The goal of thermodynamic simulation is to achieve simultaneously both decomposition of organic matter in waste and capturing hazardous radionuclides and chemical species in the finally obtained ash-slag product.

The thermochemical technology for spent IERs was developed to treat resins in a wet state[5-7]. The IERs contain a large amount of water, usually more than 50% by weight. The major radioactive contaminants of spent IERs are ^{137}Cs, ^{90}Sr, ^{60}Co, ^{106}Ru, and ^{54}Mn. In addition, spent IERs are frequently contaminated with some heavy and toxic metals. The metal powder, entering into PMF (Al, Mg, Ca, Si, etc.), reacts with water of IER and produces enough of heat to sustain the thermal destruction of IER and interaction between slags of PMF and contaminant constituents of IER. As a result, a volume of the waste decreases sharply and contaminant metals combine with PMF slags resulting chemically stable compounds.

Wet IER and PMF previously mixed in the appropriate ratio are fed into furnace where the reaction initiated and combustion occurs with the resulting release of a great quantity of heat, evaporation and gasification of IER. Air is supplied to the combustion chamber to burn out the products of IER gasification and hydrogen resulting from the reaction of the metal with the water. The process in the furnace is controlled so that radionuclides contained in the wet resin are converted into low-volatile compounds of ash residue.

Recently a mobile facility for treatment of spent ion exchange resins have been developed (Fig. 1).

Fig.1.The mobile facility for treating spent ion-exchange resins at capacity 20 kg/h.

Thermochemical treatment of organic polymer materials is performed in much the same way. In the case of chlorine-bearing polymers, chlorine of polymer and metal of PMF combine with the formation of chemical compounds remained in the slags[7].

The problem of liquidation of hazardous biological objects, for example, cadavers of animals affected by various virus and bacteriological diseases, has a great importance at present. Conventional disposal of such cadavers may generate source of epidemic in nearest future. Incineration is accepted as the best method of liquidation of hazardous biological objects. High temperatures, which ensure destroying of organics, guarantee absence of all viruses of a disease. However, incineration of animal cadavers using hydrocarbon fuels requires complicated and expensive equipment. It requires a great consumption of conventional fuel because of two-step incineration process: first, drying of a cadaver, and second, incineration proper of constituents of a biological object (proteins, fats, bony, etc.). In contrast to that application of PMF permits practically apparatus free incineration of large animal cadavers in field conditions. The consumption of PMF is rather small due to involving the water from a biological object into reactions thus ensuring one-step incineration process. The apparatus-free highly efficient technology for animal cadavers incineration under field conditions using PMF has demonstrated at a few international demonstrations with cow cadavers[8].

The performance of the method developed is governed by the active chemical interaction of the PMF with water of the biological tissue. Chemical analysis of aerosols and gases released from the reaction zone did not show excluding concentrations of nitrogen, carbon, and sulphur oxides. Analysis of ash and slags showed the absence of hazard metals, chemical compounds, and any organic substances. Remaining ash residue after cadaver/PMF incineration can be used as a fertilizer. It should be pointed that the technology proposed can be also applied to incineration of biological residues of different origin including vegetation.

Autonomous vitrification

Some specific type radioactive waste requires solidification, preferable vitrification for its safe management. An example is the ash residue obtained after solid radioactive waste incineration. Contaminated clay soils have radionuclides strongly fixed to the clay particles, which makes cleaning a complex task. This waste must be also conditioned to produce a waste form suitable for safe transportation and storage. Another type of waste that also requires conditioning before disposal is produced by water treatment facilities in the form of spent inorganic sorbents. The thermochemical processing of these wastes (ash, clay soil, inorganic sorbents, etc.) is a possible route of ensuring safe conditioning. The process is based on oxidation-reduction reactions in the PMF and radioactive waste mixture resulting significant heat generation that melts radioactive waste and forms a glass-like material without requiring an external power supply.

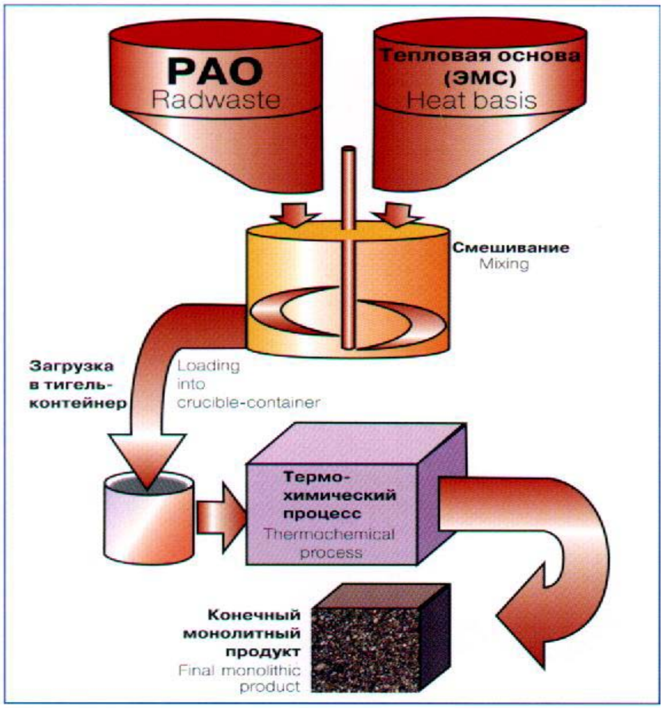

Fig.2. Schematic of self sustaining vitrification process for ashes.

Thermodynamic simulation was applied in order to design appropriate PMF formulations. Real ash residues from radioactive waste incineration as well as real contaminated clay soil were used as the conditioning objects. β,γ –emitting radionuclides of caesium, strontium, and cobalt and α-emitting radionuclides of heavy metals (actinides, radium, and polonium) were the main carriers of radioactivity in the ash residue. The radionuclides content in the soil was represented mainly by ^{137}Cs. Table II represents the parameters of both thermochemical solidification process and end glass-like product[9, 10]. The resulting materials are glass-like and have dense structure or structure with small pores.

Table II. Parameters of radioactive waste autonomic vitrification process and end product.

Radioactive waste content (wt. %)		Maximum process temperature (^{o}C)	Carry over of aerosols (wt. %)	Carry over of ^{137}Cs (%)	Leach rate (g/(cm^2))	
Ash residue	Soil				^{137}Cs	^{239}Pu
50	-	1530	1.9	0.9	$9.0\cdot10^{-6}$	$5.4\cdot10^{-6}$
60	-	1200	1.0	0.3	$7.9\cdot10^{-5}$	$7.0\cdot10^{-5}$
-	45	1900	2.2	3.1	$1.0\cdot10^{-5}$	-
-	56	1520	1.0	1.3	$2.1\cdot10^{-6}$	-

Processing of irradiated graphite

Graphite waste containing fragments of fuel and fission products were accumulated mainly during operation of uranium–graphite reactors. The ^{14}C-content in reactor graphite may be as much as 1 wt.%. For safe disposal and long-term storage, such waste must be properly processed into chemically stable materials. Other carbon containing (including ^{14}C radionuclide) wastes are subject of special attention. Incineration of irradiated carbon is impermissible because of discharge into atmosphere of biologically significant isotope ^{14}C combined in $^{14}CO_2$ and ^{14}CO. For treating ^{14}C-containing waste a thermochemical treatment technology was developed based on the self-sustaining exothermic reaction in the mixture of carbon (graphite), aluminium, and titanium dioxide[11, 12].

Fig. 3. Thermochemical processing of graphite.
Left – ignition, Centre – process occurrence, Right – final product.

The thermochemical processing of graphite is carried out in a neutral (argon) atmosphere. A mixture of PMF with powdered graphite is placed into a crucible-container where the self-sustaining synthesis reaction is ignited (Fig. 3, left photo). The self-sustaining process occurs with a release of a substantial amount of heat; temperatures higher than 1700 ^{O}C are achieved. Nevertheless the carry over of carbon is minimised to values as $10^{-4}/10^{-7}$ for CO and CO_2 respectively. The self-sustaining reactions result in chemically stable titanium carbide – corundum matrix acceptable for long-term storage and disposal.

Processing of irradiated zirconium

Immobilization problems for radioactive zirconium waste are also topical. Considering that zirconium has a high calorific power, a self-sustaining reaction would also be appropriate for its treatment. The feasibility of this method was investigated using both thermodynamic analysis and experiment[12].

In thermodynamic calculations, metal zirconium and aluminium, zirconium, titanium, manganese, and barium dioxides, potassium permanganate, calcium oxide, and other were chosen as source components for self-sustaining reactions of zirconium treatment. The calculation showed that the end product of exothermic self-sustaining reactions consists of complex oxides together with calcium and barium titanates and zirconates as well as spinel predominating. The equilibrium reaction temperatures calculated are reached above 2100 K.

By precursors combination, the optimal mixtures were selected using thermodynamic simulation, resulting the maximum titanates and zirconates content in the end product, minimum gas phase outlet, and absence of hazardous substances.

We could not perform a more detailed thermodynamic investigation of zirconium-based systems due to an absence of thermodynamic properties of a wide variety of zirconium-bearing substances and minerals.

An experimental bench-scale verification of thermodynamic analysis results has been also carried out. Experiments were conducted in an argon atmosphere as well as under ambient atmosphere conditions. Self-sustaining exothermic reactions, involving zirconium, proceed very actively, a violent melt boiling occurs. Starting mixtures were loaded with inert filling agents, such as alumina, titanium dioxide, zirconia, and the end product powder, to reduce process intensity. The end products provide a fine-porous, monolithic, ceramic-like, and dark-coloured material.

The samples produced were examined by scanning electron microscopy equipped with energy dispersive system and by XRD. It has been found that the samples, resulting from the starting mixtures without calcium compounds addition, have crystalline structures and consist of three phases (Fig. 4).

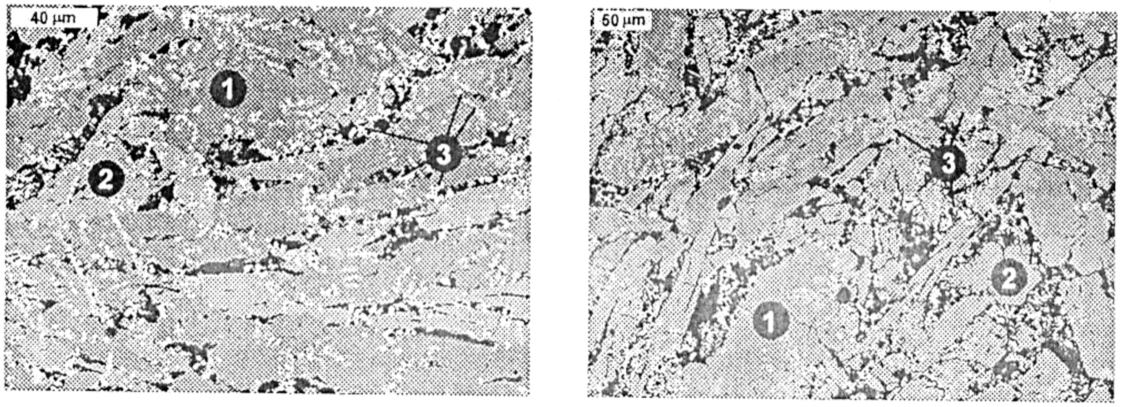

Fig. 4. SEM-patterns of zirconium processing samples produced in an argon (left) and air (right) atmosphere.

Two phases, being $Ba_{0.50}K_{0.28}Mn_{1.53}Al_{0.75}Ti_{6.07}Zr_{0.29}O_{16.00}$ and $Ba_{0.84}K_{0.50}Al_{0.25}Ti_{6.78}Zr_{0.48}O_{16.0}$ in composition (1 and 2 respectively in Fig. 4), are closely consistent with theoretical chemical formulae of hollandite mineral crystal group AB_8O_{16}, in which the large Ba^{2+}, K^+, Cs^+ cations occupies the A-positions and polyvalence transition metals Mn, Co, Ni, Ti, Al occupies the B-positions. The crystal plane distances defined with XRD method agree well with those of the natural mineral priderite $(K,Ba)(Ti,Fe)_8O_{16}$. Hence, these two phases may be considered as complex titanates of hollandite group. Zirconia dominates in third phase (3 in Fig. 4). Dimensions of zirconia particles are too microscopic. As a consequence, it was not possible to distinguish zirconia from elements impurities captured from ambient first and second phases. In addition, some unidentified peaks of relatively high intensity were found on XRD-diagrams, suggesting evidence of extremely small phase grains (no more than 1 µm) or aggregates at these grains with baddeleyite / hollandite phases.

The samples, resulting in an argon and air atmosphere (Fig. 4, left and right respectively), are a somewhat different. In the argon atmosphere case, the hollandite phase is dominated and zirconia is at secondary importance. In the air atmosphere case, the ZiO_2–content is significantly increased but remains negligible.

By adding calcium oxide into starting mixture, the crystal perovskite $CaTiO_3$ and a number of unknown substances with intensive XRD-peaks are formed in the end product.

Conclusion

High efficient thermochemical treatment technologies were developed to process specific type radioactive wastes. They are rather simple in implementation and can be realized without complex production equipment and energy supply.

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