RADIOACTIVE WASTE TREATMENT TECHNOLOGY AT CZECH NUCLEAR POWER PLANTS

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Abstract

This presentation describes the main technologies for the treatment and conditioning of radioactive wastes at Czech nuclear power plants. The main technologies are bituminisation for liquid radioactive wastes and supercompaction for solid radioactive wastes.

1. INTRODUCTION

By the term of *waste* we usually understand a thing, of which its owner (waste producer) wants to dispose. Waste might also be some movable material, the disposal of which is necessary to protect human health and the environment, even when the producer of the waste is unknown.

Radioactive waste from nuclear power plants (NPPs) include materials and equipment, which are not possible to be introduced into the environment due to radionuclide content or unremovable surface radioactive contamination. For that reason, their handling is controlled by special procedures (processing, treatment, transport). The boundary between radioactive waste and other waste is not precise. Discharge limits for release of radioactive materials into the environment, have been adopted by the competent authority (SONS).

Radioactive waste arises during maintenance and operational activities in radioactive environments. Radioactive waste arising in a NPP may have specific activity up to 10^8 Bq/kg with about 30 year half-life.

2. OBJECTIVE OF RADIOACTIVE WASTE HANDLING AT DUKOVANY NPP

The main objective of waste management is to isolate radioactive waste from the environment.

Radwastes from normal Dukovany NPP operation are disposed of in a surface disposal facility on Dukovany NPP site. The basic objective is to isolate waste from environment for about 300 years, which correspond to 10 half-lives of the dominant radionuclide (^{137}Cs). This decay period results in an activity reduction by 3 orders of magnitude (i.e. from 10^8 to 10^5 Bq/kg). Waste has to be in a suitable form for disposal prior its deposition in the disposal facility.

2.1. Minimization principle

An important principle of radioactive waste treatment is its minimization, which is a process leading to the smallest practical amounts of treated waste. Keeping waste quantities low has economic, environmental and political advantages. It is also very important for public acceptance. For that reason, it is useful to give examples of possible additional waste reduction:

- recycling boric acid from liquid waste,
- treating low activity waste to reduce chemical content (water is recycled),
- release of decontaminated metal (the volume of treated decontamination solutions must not exceed metal volume for recycling),
- optimization and selection of chemicals used in controlled area to minimize foaming in evaporator (shampoo, soap, washing powder, cleansing powder, floor detergents, etc.). Foaming in evaporator can cause premature saturation of deminaralizer resin capacity,
- avoid bringing unnecessary objects into the controlled area (packages),
- avoid unnecessary entry of persons,
- usage of thinner (lighter) foils as protection against contamination,

- usage of optimum concentrations of drained media (i.e., usage of 12,8% boric acid instead of 12% increases volume of chemicals in wastewater above the level necessary during maintenance),
- replacement of service water by condensate or demineralized water in areas with leakage (reduction of salt volume in condensates).

3. CATEGORIZATION OF WASTE — RADWASTE CATALOGUE

Categories of wastes from the Dukovany NPP classified from the technical point of view are given in Table I.

TABLE I. CATEGORIES ACCORDING TO WHICH WASTES FROM DUKOVANY NPP ARE CLASSIFIED

No	Category	Waste characteristics	Source	Technology of treatment	One-year Production (t/y)	Activity (MBq/kg)
1	Compactible/ Combustible	Condemned personal protective aids, decontamination and cleaning clothes, packing materials, paper, PE sheets	the biggest part originates during unit inspections and repairs	high-pressure compaction, combustion	20	1-2
2	non-combustible	glass, wires, cans, metal particles, ceramics, filters	mainly during inspections and repairs	high-pressure compaction	3	1-2
3	wood	wooden transport packages, pallets, scaffold flooring, planks	contingent origination, air-conditioning filters replacement	high-pressure compaction, combustion	1	0,1
4	Flammable but unfit for combustion	PVC, PTFE (teflon) - foils, sealing materials	previously extensively used materials in RCA	high-pressure compaction	1	0-1
5	Large metal objects	Structural material of carbon and stainless steel	Extensive reconstructions	disposal without treatment or decontamination and recycling	10	0,01
6	Resins	Condemned purification station fillings	regular substance replacement, contingent leakage during technological operations	insertion into HIC[a], bitumenisation	30	100
7	Other sorbents	active coal, vapex (perlite), zeolites	--"--	insertion into HIC, cementing	1	not given
8	Sludge	Sediments in tanks, mixture of organic and inorganic substances of non-standard composition	floor washing and cleaning, dust from material separation and abrasion, crystallization beyond design basis	insertion into HIC, cementing	5	10
9	wastewater	usually diluted solutions of chemical inorganic substances containing impurities	Uncontrolled leakage, sampling, laboratory water, spilling of liquids	concentrate bitumenisation	350	1
10	Oils and solvents	Depreciated lubricants, solution residues and scintillators	filling exchange, laboratories, elimination of non-applicable and contaminated liquids	washing by demineralized water, combustion	2	0,001
11	Ash, fly ash, slag	residues after combustion and melting	external incinerator, melting furnace	insertion into HIC, cementing	0	not given

[a] HIC means high integrity container

4. METHODOLOGY OF RADWASTE PROCESSING AND TREATMENT

4.1. Processing and treatment of liquid radwastes

4.1.1. Origination and composition of liquid radwastes

The following main sources of liquid radwastes at Dukovany NPP need to be considered:

- Recovery solutions and purification plant flushing,
- Liquids collected in plant systems,
- Decontaminating solutions,
- Wastewater from laundry and water from changing rooms if it is not possible to discharge it to sewage drainage from the radiation point of view,
- Alkaline agents for radioactive concentrate stabilization.

According to purification plant type, recovery solutions and purification plant flushings contain nitrates (from cation resin recovery by nitric acid), borates (boric acid washed out from highly basic anion exchanger), potassium hydroxide, sodium hydroxide and ammonia (from anion exchanger recovery). In highly reducing conditions nitrates also arise.

Liquids collected in drain systems contain salts from primary coolant circuit and salts originating in service and cooling water, with sulphate, chloride and calcium content. A substantial part of this kind of wastewater originates in the course of unit outages during drainage of pipelines and tanks. Intakes to the drainage system are then a significant source of wastewater organic pollution (cleaning and others).

Decontamination solutions contain particularly salts of manganese (reduction of $KMnO_4$ used in alkaline decontamination solution), sodium and potassium and residues of citric acid and oxalic acid which are, however, in the given environment, rather unstable.

Laundry wastewater and changing room water usually do not represent a significant part of wastewater because they are discharged, if their activity is low, to the inactive sewage system of Dukovany NPP. If it is necessary to treat them with radioactive water, they introduce surfactants, phosphates and increased organic pollution with to the treatment systems.

Alkaline agents are added before entering the evaporator prior to wastewater concentration.

4.1.2 Collection, concentration and storage of liquid radwastes

The primary section of Dukovany NPP is equipped with a unified sewage system. The main disadvantage of this system is mixing of all sorts of wastewater and therefore recycling of separate wastewater is complicated and difficult.

This unified sewage system is routed from the twin unit 1 to radioactive drain sump tanks and wastewater is pumped from there to a sedimentation tank located in the auxiliary service building and then through an overflow tank to wastewater holdup tanks.

Wastewater from laundry, laboratories and changing rooms of operational building 1 is collected in control tanks and if it is not possible to discharge it, it is pumped to the radioactive drain sump tanks.

Regenerative and flushing water are routed through a tank to the radioactive drain sump tank, and from there to the overflow tank and then by the same path as the rest of water to the wastewater holdup tanks.

The situation of the twin unit 2 is similar.

Wastewater in the wastewater holdup tanks is analyzed to determine the need for further concentration in evaporators. Usually it contains 0.5–2 g of salt/l with pH ca. 8. Crystallization of borates with relatively low solubility might occur during cool down, storage or other handling in neutral and acid media. Prior to concentration, it is necessary to alkalize this wastewater by addition of sodium hydroxide to pH at least 11 to reach solubility 60 g of boric acid/l.

Evaporation is used to concentrate the salt concentration in waste liquid about 50 times. The concentrated residue is pumped to concentrate tanks. Both auxiliary service buildings are inter-connected through three pipelines for liquid radwastes and they are surrounded by a protective trough.

Composition of concentrate changes both with time and between individual NPP units depending particularly on unit mode.

In the following table (Table II) is a typical composition of RA concentrates produced at Dukovany NPP.

TABLE II. TYPICAL COMPOSITION OF WASTES AT DUKOVANY NPP

PH		11,4
Specific weight	kg/m^3	1110
Salt contents	g/l	147
Boric acid	g/l	65
Nitrates	g/l	30
Nitrites	g/l	2
Sulfates	g/l	3
Chlorides	g/l	3
Oxalates	g/l	2
Citranes	g/l	1
Sodium	g/l	35
Potassium	g/l	6
134-Cs	kBq/l	300
137-Cs	kBq/l	400
58-Co	kBq/l	10
60-Co	kBq/l	60
90-Sr	Bq/l	10
239+240 Pu	mBq/l	200

Since saturated solution is introduced into the condensate storage tanks, it means that boric acid salts crystallize out on the bottom, vessel internals and the like. When the temperature or pH value increases, they gradually go back into solution.

The aim of chemical operation control during concentration is to reach purposely maximum concentration (to minimize volume) but without exceeding the solubility limit of salts present, particularly borates. This problem is not simple. Disposal of crystallized salts is very demanding from the technical and economical point of view.

4.1.3. Liquid concentrate treatment

The objective of liquid radioactive concentrate treatment is to transform it to a form suitable for disposal. Such a form has to be a solid state and therefore we often talk about liquid waste solidification.

Two basic technologies are mainly used for this purpose in the case of nuclear power plant wastes:

- cementation,
- bituminisation.

In the future, it might be that technology used to date for high-level radioactive waste solidification from reprocessing plants could be applied to NPP wastes-vitrification.

Cementation is a relatively simple technology is based on chemical reaction of mineral components, contained in cement, with water. This reaction is called hydration. Water is chemically combined in the final product — with a certain fixation ability for radionuclides contained in charge water. It is evident that the mass ratio of water to cement is not unlimited and the maximum for solid product is usually about 0.4. As a result, waste volume and weight increase significantly during this process. Another disadvantage is relatively high leachability, that is, release of fixed components from the product in the case of contact with water.

Bituminisation consists in fixing of contaminated salts into a water resistant matrix, using asphalt. During the process of liquid radwaste bituminisation water evaporates with temperatures above 120°C and contained salts are homogenized with asphalt.

During vitrification, the process, the waste material is melted at temperatures about 1000°C with glass-forming material, resulting in a product with very low leachability. The volume reduction is very good.

4.1.4. Bituminisation at Dukovany NPP

Liquid radwaste bituminisation is the process used in the Dukovany radioactive waste treatment facility. The basic equipment is a layer rotor evaporator with a vertical double-shell drum of inside diameter 600 mm, made from molybdenum steel, for 1.1 MPa steam heating. Fitted in the axis is a shaft with swinging blades that in radial direction nearly touch the internal surface of the heated shell. Asphalt and liquid concentrate are tangentially sprayed to the upper part of evaporator. The function of the blades is to spread the mixture on the internal heated surface during the rotor revolution (300 rev./hour) and so create a thin layer from which water evaporates and residual salts are mixed with asphalt. Drained bitumen product, containing ca. 40% of mass salts, flows down the evaporator wall and continues through heated piping to drums where it is lidded automatically and then transported to the disposal facility. Theoretical capacity of the evaporator is 240 liters per hour.

Concentrate is transported to the radioactive waste treatment facility building from the tanks located in the auxiliary service building jusses or directly by a submersible sump pump from the storage tank. The tanks, each of 7 m^3 effective volume, are filled through this pump. There is also the possibility of pH regulation by nitric acid or sodium hydroxide addition in these tanks. Required pH values, according to technical specifications, is 11–11.5. The lower value is to avoid crystallization and the upper value prevents so called asphalt alkaline pyrolysis, which is exothermic reaction of organic components at higher temperature in asphalt with high pH values and with multivalent metal catalysis. Manganese content is limited to 15 g/l for the same reason.

Asphalt is transported to Dukovany NPP by trailer and is stored with temperature of ca 120°C in a tank located outside the radioactive waste treatment facility building. It is very important to select an asphalt type carefully because product quality depends on it (softening point, penetration, leachability). Some asphalt types are inclined to carbon and hard substances insoluble in common organic solvents and non-fusible by on site temperatures. Then pipeline fouling and evaporator vibration occur. To eliminate these problems, various additives are added to asphalt at Dukovany NPP.

Asphalt is pumped from the storage tank through steam heated pipelines to a tank and from there it is sprayed by heated gear feed pumps to the evaporator. Feed is regulated in such a way to reach 40 mass % of salt contents in the resulting product, which means that a feed rate of ca 50–60 kg of asphalt/hour.

4.2. Solid radwaste processing and treatment

Solid radwastes at Dukovany NPP are produced principally during refuelling and maintenance. Solid radwaste processing involves collecting, sorting, bagging and storing of radioactive waste. Bags of waste are classified according to radioactivity content.

Waste bags with surface dose rate lower than 1 µGy/h are sorted in a storage carousel. These bags are assumed to be inactive and can be released as normal trash. Before disposal, they are additionally sorted with respect to materials to paper (scrap), other combustible waste (clothes and plastics) and metal.

Waste bags with surface dose rate higher than 100 µGy/h are more radioactive. Non-compactible objects are removed and they are stored for several years.

Waste bags with dose rate 1-100 µGy/h are low active. Since their activity might be caused only by one object it is worthwhile to sort these bags according to their activity. Sorting is performed in a semi-automatic sorting box and it enables operating personnel reliable separation of radwastes and inactive wastes. Solid radwastes produced by this sorting are stored together with radwastes of higher dose rates and inactive wastes are removed again.

Dukovany NPP does not have equipment for further routine solid waste treatment. The sorted radwaste bags are stored in reinforced concrete cells pending periodic treatment campaigns using high pressure compaction.

During the campaigns performed about every ten years, the stored radwastes are removed, then treated by compaction and placed into radioactive waste disposal. Treatment is performed in two stages. Bags with compactible waste are gradually inserted into drums and low-pressure compacted. Low-pressure non-compactible wastes (small metal, glass, etc.) are inserted into drums without compacting. Low-pressure compaction of up to 15 waste bags (50 l each) in one 200 l drum is possible. When the drums are full they are transported to a high-pressure compactor operated by a contractor (IAEA technology). About 2500 filled drums were re-compacted with super press AEA (Great Britain) in 1996. Moulded cakes were inserted into 820 larger drums and they were disposed in radioactive waste disposal.

The following objects are not suitable for high-pressure compacting in AEA device:

- Drums with weight above 300 kg,
- Drums with dose rate above 3 mSv/h,

- Drums dimensionally unfit,
- Wet or highly oiled up wastes,
- Toxic wastes,
- Metal waste longer than 550 mm and 60–250 mm in diameter,
- Pulverized waste,
- Wastes containing significant volume of plutonium, uranium, americium and tritium.

Combustion is often used for solid radwaste treatment in foreign countries. The higher volume reduction is reached by combustion. Organic substance destruction prevents subsequent microbial decomposition and gas production. Disadvantages of radwaste combustion are both inaccessibility in the Czech Republic, high price and also necessity of ash treatment (by cementing, sintering, vitrification). It is usually effective to use low-active waste technologies for metal decontamination (half-dry decontamination). If the metal is too highly contaminated, fragmented metal is stored in the drums without treatment. It is possible to place large metal parts in the radioactive waste disposal facility as non-standard radwaste, but extra permission is necessary. Contaminated metal melting is used during NPP decommissioning in foreign countries but this process is very expensive considering the negligible quantity of contaminated metals at Dukovany NPP.

4.3. Treatment of other radwastes

4.3.1. Moist radwaste

Exhausted contaminated ion exchangers are taken out of service from purification plants at Dukovany NPP. Ion exchange resins are usually in the form of small beads (smaller than 1 mm) with capacity to capture ions and impurities from solutions. Filters might contain other media such as activated charcoal, perlite or even sand. Contaminated sludges are radioactive wastes of valuable composition. They originate from impurities, from condensation of chemical substances or crystallization of saturated solutions. They contain variable water percentage. They are called, together with ion exchange resins and other sorbents, as "moist radwastes". Moist radwastes are usually transported by water flow with the help of pumps. Their treatment for disposal is only being planned so far. They might be cemented, calcined, bituminized, vitrified, or they might be disposed of without a matrix. This particular method has been chosen for application at Dukovany NPP. The wastes are pumped into a special container without sorting or any other treatment and dehydrated. This leak proof container, known as a HIC (high integrity container) represents a multi-layer barrier against radionuclide release. Waste dried by vacuum pump is of minimum volume because it is not mixed with binder (cement, bitumen). Water resistance is provided by the container maintaining its leak tightness for about 400 years. Moist radwastes might attain high activity (up to 10^9 Bq/kg). High activity and atypical size of HIC containers might represent certain problems with manipulation. Non-standard composition, which might cause difficulties for some technologies due to changeable additive composition, is not a problem for HIC technology.

4.3.2. Oils and solvents

Oily substances, that are also in stable form classified as hazardous wastes, are involved as a rule. Radioactive oils are usually burnt in foreign countries. This method will presumably be used for radwaste disposal at Dukovany NPP and this activity will be provided by contractor (i.e. incinerator). Oils have been treated in the past at Dukovany NPP by liquid-liquid extraction. The method consists in extraction of radioactive substances by demineralized water. A mixture of oil and water is sucked by a pump into a closed vessel. After some hours the phase equilibrium is established and water discharged from the lower part of the vessel. The water contains radioactive substances and it is treated in purification system. After repeated extraction, oil is recycled as inactive waste. During oil collection it is necessary to segregate certain oils. The most important consideration is not to mix the most toxic oil substances (containing PCB and the like) with the rest of oils. It is very important to store non-chlorinated oils separately from chlorinated substances because burning of mixtures is very expensive in the case of chlorinated contents. Individual sorts of oils are also not mixed, if it is possible, due to viscosity changes.

It is possible to decontaminate solvents through extraction but also through distillation. Only distillation of perchlorethylene used in the radioactive waste treatment bituminisation line has been performed at Dukovany NPP

4.3.3. Ash, fly ash and slag

These radwastes may arise if Dukovany NPP contracts for incineration or melting of wastes in the foreign countries in the future. However, the most probable case is that the contractor will treat these wastes with the use of cement technology and return them in our 200 l drums or put them into our HIC casks.