TREATMENT AND CONDITIONING OF AQUEOUS EFFLUENTS FROM LWR'S

OPTIMIZATION IN VOLUME REDUCTION AND INSOLUBILIZATION

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ABSTRACT

Evaporator bottoms resulting from the treatment of aqueous effluents from PWR's and BWR's can be treated by chemical means and the resulting sludges can be further conditioned by cementation, bituminization or high temperature slagging. As compared with the reference process (direct cementation), the chemical treatment and conditioning processes lead to additional volume reductions to less than 10%. After high temperature slagging and mixing with an adequate matrix material, the total cumulated amount eluted, may be reduced to less than 0.1% of the contained radioactivity.

INTRODUCTION

With regard to treatment and conditioning of radioactive wastes, particular attention is being spent in Belgium to the end volume and the characteristics of the conditioned products in view of their disposal. The present study is devoted to some aspects of treatment and conditioning of aqueous effluents from LWR's.

In most LWR power stations, aqueous effluents are currently being treated by evaporation followed by solidification of the concentrate (evaporator bottom) with cement.

The treatment and conditioning scheme promoted by SCK/CEN-Mol aims at the optimisation of the final volume (reduction) and stability (chemical, physical, ...) of the conditioned end-product. It is based on the following simple principles :

(i) separation of the water and the bulk of the dissolved non-hazardous components (nitrate, sulfate, borate, ...) from the radioactive constituents; this is mainly achieved by chemical and physico-chemical treatment;
(ii) release into the environment of the purified effluent containing also the non hazardous chemical components;
(iii) adequate conditioning of the separated fraction of radioactive sludge by a conventional process (cement or bitumen) or a more advanced one (thermosetting resin or high temperature slagging).

This approach has been in use at CEN/SCK since the late sixties; it has also been practiced on behalf of the National Radioactive Waste Agency (NIRAS/-ONDRAF) and utilities from Belgium and the FRG for the treatment/conditioning of the evaporator bottoms produced by the latter power stations.
The purpose of this paper is to give a very brief description of the methods and processes used for the treatment and conditioning; a section has been added in which other factors e.g. leach rates and impact on the environment and disposal costs are briefly commented.

TREATMENT AND CONDITIONING PROCESSES

Characteristics of the Evaporator Bottoms

The evaporator bottoms considered here result from evaporation of various kinds of liquid service effluents (floor drains, etc...), chemical regeneration effluents and borated waste streams.

On the average, a 1 GW(e) power station may produce between 20 and 200 m^3 of such evaporator bottoms per year with the following average composition.

- boron : 60 $g.l^{-1}$ (for PWR's)
- sulfate and other dissolved solids : 200 $g.l^{-1}$ (for BWR's)
- radioactive contaminants: 30 $GBq.m^{-3}$, mainly ^{60}Co and ^{137}Cs
- in some cases, the concentrate may also contain strong complexing agents and various organic components.

As was mentioned before these evaporator bottoms are currently solified with cement; at CEN/SCK-Mol tests have also been done for the direct bituminisation of these concentrates;however the main effort has been devoted to the development of an alternative route which is described below and is based upon :

- chemical and/or physicochemical treatment
- conditioning of the resulting chemical slurry.

Chemical Processes

Taking into account the variety in composition of the evaporator bottoms, largely dependent upon their origin, it is clear that optimum results (decontamination and volume reduction) should not be expected from the systematic application of only one type of chemical treatment process. Essentially the presence of chelating agents and other decontamination agents may require the application of one or more chemical processes. They are described briefly :

a. Ferrouscyanide process

This process is a combined one-step system composed of :
- pH adjustment to 4
- addition of $FeCl_3$ or $Fe_2(SO_4)_3$
- addition of $K_4Fe(CN)6$ and $CuSO_4$
- addition of $BaCO_3$
- pH adjustment to approx. 9

In case of presence of chelating agents, a preliminary oxidation step with $KMnO_4$ may be required.
The decontamination factor obtained is usually of the order of 100 and the amount of precipitate produced is of 200 g dry matter per m^3 of evaporate bottom.

b. SDEC Process

Mainly for effluents with very high concentrations in chelating agents a process is used based on the application of the precipitating agent Sodiumdiethyldithiocarbamate (for cobalt complexes) in the following sequence :
- oxidation with H_2O_2
- treatment with Na_2S and SDEC
- treatment with copper hexacyanoferrate(II)
- possibly followed by treatment with $BaCO_3$

The decontamination factors obtained are currently between 20 and 90

c. Other processes

Other processes may also occasionally be used. Their purpose is to precondition the evaporate bottom in view of the application of the main chemical precipitation processes. One technique of preconditioning is based upon electrolytic oxidation.

The above described processes are applied after careful characterization of the effluent which helps in deciding the sequence of the chemical operations, the concentration of chemicals, etc....

Conditioning Processes

The sludges produced during the treatment process are further concentrated. The so predried sludge is finally conditioned by one of the following methods:

Conditioning Process	Sludge (TDS) per ton of final product
Concrete	200 - 400 kg
Bituminization	200 - 400 kg
Thermo setting resins (laboratory scale)	200 - 400 kg
High temperature slagging	200 - 300 kg

In the high temperature slagging incinerator (HTSI) the final product (slag-granules) contains mineral material collected in the liquid effluent treatment process and ashes resulting from the incineration of various combustible and non combustible wastes.

RESULTS

During the past 5 years, 1,500 m^3 of evaporator bottoms from several domestic and foreign nuclear power stations have been treated. The results are expressed in:

- volume reduction
- leach rate and environmental impact

Volume Reduction

For a reference volume of 100 m^3 of evaporator bottom, which roughly corresponds to the yearly volume of aqueous concentrate produced by a 1 GW(e) nuclear power station, the following average figures have been recorded; the composition is given.

Combined Treatment and Conditioning	Volume of final conditioned material
- direct cementation of the evaporator bottom	250 m^3
- direct bituminisation of the evaporator bottoms	80 m^3
- chemical and physico-chemical treatment (as described in 2.2.) followed by :	
. cementation	8 to 24 m^3
. bituminisation	2,5 to 15 m^3
. high temperature slagging	4 to 20 m^3

In the case of high temperature slagging it should be remarked that the slag contains both ashes and chemical pricipitates from the treatment of the evaporator bottoms.

According to the above figures, the application of the more advanced treatment and conditioning processes leads to savings of more than 90% on costs of transportation and disposal of the end products; these savings are to be weighed against the supplementary costs of treatment and conditioning.

Leach Rate

Leach rates (in water at 20°C) of the various waste end-products, referred to earlier, have been established. Taking also into account specific surface of these waste forms, the following results have been obtained. (See table).

TABLE I

Treatment of the Evaporator bottoms	Conditioning	Characteristics of the end product $S(cm^2.g^{-1})$	$L(g.cm^{-2}\ d^{-1})$	% eluted ^{60}Co after 30 y	^{137}Cs after 100 y
no	concrete	2,1. E-2	1,- E-3	5,6	77,3
	bitumen	5,3. E-2	1,- E-4	1,4	45,4
chemical treatment	concrete	2,1. E-2	1,- E-3	5,6	77,3
	bitumen	5,3. E-2	3,1 E-5	0,5	20,1
chemical treatment + High temperature slagging	no	4,8. E+0	3,1 E-6	4,-	70,7
	hot-pressed	3,0. E-2	3,1 E-6	0,02	1,3
	concrete	2,1. E-2	3,1 E-6	0,02	1,-
	bitumen	5,3. E-2	1,- E-7	0,001	0,08

It may be assumed that, for a nuclear power plant (LWR) of 1 GW(e), the evaporator bottoms contain on the order of 2 TBq (50 curies) of radioactivity, 70% ^{60}Co and 30% ^{137}Cs. For the best combination (chemical treatment - high temperature slagging - bitumen) it seems worthwhile to examine whether and to which extent such materials may be disposed off in shallow ground, even in a humid environment.

REFERENCES

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