DECONTAMINATION OF RADIOACTIVE WASTE WATER BY CHEMICAL PRECIPITATION AND CENTRIFUGATION

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ABSTRACT

At the end of 1984, BWB Engineering GmbH, Lörrach/West Germany, was assigned the task of planning and supplying a complete plant for the treatment of radioactive contaminated waste water by chemical precipitation, subsequent centrifugation and solidification. The plant has to be incorporated in a nuclear power plant, operating with two pressurized water reactors (PWR), design Westinghouse.

The report deals with the previous decontamination methods and the development of new techniques to improve the results, as well as fulfilling the various safety requirements in the realization of this complex project.

The said plant is scheduled to be commissioned in May 1987. The operating results will be published at a later date.

INTRODUCTION

The nuclear power station Beznau (KKB) in Switzerland, which operates with two pressurized water reactors (KKB I and KKB II of 350 MWe each) was seeking a better solution to the problem of treating their contaminated waste water.

In the past, the low to medium active waste water, which is mainly produced when changing the fuel elements and during decontamination, was concentrated in evaporators and the resulting concentrate subsequently solidified.

In order to offer a better solution to this problem, a process was developed, which decontaminates the water by chemical precipitation and subsequent centrifugation. As compared with the results obtained with the existing evaporators, the new method does not only increase the volume reduction by a factor of 10 but also increases the decontamination effect by a factor of 10.

Lay-out of the Present Plant

The nuclear power plant consists of two blocks, the first (KKB I) was taken into operation in 1969 and the second (KKB II) in 1971.

In the past, the accumulating contaminated waste water was collected in tanks and, according to the degree of contamination, was fed by two different methods into the draining ditch:

1) When the level of contamination was below the maximum level, laid down by the authorities, the water was simply passed through a filter to remove the suspended substances and subsequently fed into the draining ditch.

2) If, however, the degree of contamination exceeded the permissible level, the waste water was concentrated in residue evaporators. After being examined, the condensate was then fed into the draining ditch, whereas the concentrate was conveyed into a solidification plant. (Fig. 1)

The residue evaporator, an old-fashioned single-effect sea water evaporator, had the following shortcomings after being in operation for 15 years:

- poor decontamination factor
- tendency to cause foaming
- susceptible to breakdowns
- problems with corrosion
- low capacity

The result was a very restricted usability. Furthermore, the relatively low solubility of the boric acid in the concentrate indirectly impaired the reduction of its volume. During the subsequent cementing of the concentrate, it became evident that the restricted absorption properties of the cement in relation to the boric acid, created a relatively high radioactive waste volume.

A more developed evaporator design could reduce the above mentioned disadvantages. However, due to space constraints, a replacement of the existing compact evaporator by a more sophisticated one, would have been impossible. Therefore, it was decided that a new method must be found with the following objectives:

- improvement of the decontamination factor
- reduction of the volume of the radioactive waste

The Development of a New Process Technology

The task at hand was to find a simple, easily applicable method of decontaminating approximately 1000 m^3/year, produced by the two PWR's, consisting of low and medium active waste water and composed roughly as follows:

σ-radioactivity	10^{-4} to 10^{-1} Ci/m^3
pH	7 - 9
Content of boric acid	100 to 1000 ppm Bor = 0,06 - 0,6 % H_3BO_3
Insoluble solids	up to 1 g/l (mainly magnetite)

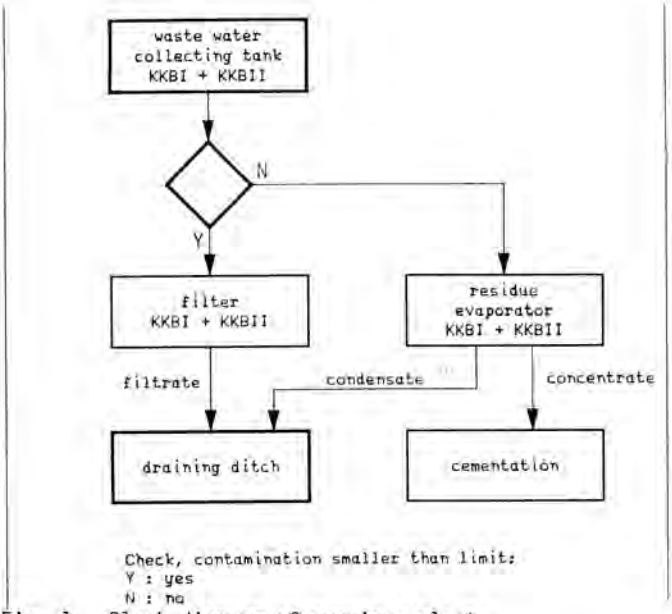

Fig. 1. Block diagram of previous plant.

The radioactivity of the water is composed of over 90% of nuclides Co-58/90 and Cs-134/137.

After extensive research, the idea of precipitation was born. Based on the knowledge that the chemical and radiochemical composition of radioactive waste water, produced by a nuclear power station, varies only within very narrow limits and bearing in mind that only a method of precipitation could be considered, that would also remove the Cs-isotopes dissolved in water, perhaps by coprecipitation or adsorption; it was decided that a series of laboratory experiments should be carried out, based on the research work done by Krawczynski and Kanellakopoulos (1).

The pH-values are requested to be in the region between 6,5 and 8,5 when being fed into the draining ditch. Thus, in order to avoid a further process step, namely neutralization, the heavy-metal salts of the ferrocyanide are supposed to reach a maximum decontamination factor for Cs in this pH range. The iron(III) ferrocyanide (Berlin Blue) (Fig. 2) fulfills this demand. The formation of iron(III)hydroxide with its low solubility is regarded here as a favorable side-effect. Therefore, the suitability of the precipitation method described in (1) was only examined near the second decontamination maximum (pH 7,5).

The following chemical equation served as a basis for the tests described in (2):

$$3\ K_4(Fe(CN_6) + 4\ FeCl_3 \text{ -- } Fe_4(Fe(CN)_6)_3 + 12\ KCL$$

potassium ferrocyanide — iron(III) chloride — Berlin Blue — potassium chloride

resulting in a standard precipitation procedure consisting of 6 steps:

Step 1 setting the pH value at 2 to 3
Step 2 addition of $8 \cdot 10^{-4}$ Mol/l $K_4(Fe(CN)_6)$
Step 3 addition of $2{,}4 \cdot 10^{-4}$ Mol/l $FeCL_3$
Step 4 neutralization with $Ca(OH)_2$ to between pH and 7,5
Step 5 stirring for one hour
Step 6 removing the precipitate by centrifugation

When using iodine isotopes, possibly deriving from a coolant leakage or faulty fuel elements, the standard precipitation method can be supplemented by adding a silver iodide precipitation after Step 1.

Step Ia addition of 10^{-5} Mol/l KJ
Step Ib addition of 10^{-3} Mol/l $AgNO_3$
Step Ic storring for 3 hours

During the official approbation procedures, the authorities pointed out that the resulting iron content was considered as too high. It was back to the laboratory, therefore, this time to conduct tests under the first decontamination maximum (pH 4,5). The resulting iron content was finally lower than the threshold value laid down by the authorities. The input of slightly acidic water into the draining ditch was also approved, all the more so since this would serve to reduce the pH value of the slightly alkaline draining ditch.

Test Results (2)

The standard precipitation method served to decontaminate radioactive water of various degrees of activity concentration and nuclide composition accumulating in a PWR. The test results are shown in Table I.

The test solutions No. 1 to No. 4 are typical examples of radioactive waste water, such as occurs in the nuclear power station at Bexnau. The decontamination factors (DF) that were reached are between 100 and 1000, depending on the activity concentration in the waste water. The sum of scale values (denoting the ratio of activity concentration to maximum level tolerated in drinking water of a specific nuclide) in the water, decontaminated by chemical precipitation is below 0,3. The emission, therefore, is at least 30 times below the emission limit of 10 scale values.

The test solution No. 5 used is a concentrate from the residue evaporator with 14000 ppm Bor. The nuclide Ag 110m and Sb 125 were removed with a decontamination factor of only 8 and 25 respectively. The decontamination factor of all other nuclides was between 100 and 2200.

The test solution No. 6 is a degassed primary coolant with an activity of J131/J133 of $7.0 \cdot 10\text{-}3$ Ci/m^3 (3 days old). In order to remove the iodine activity, a silver iodide precipitation was added to the standard

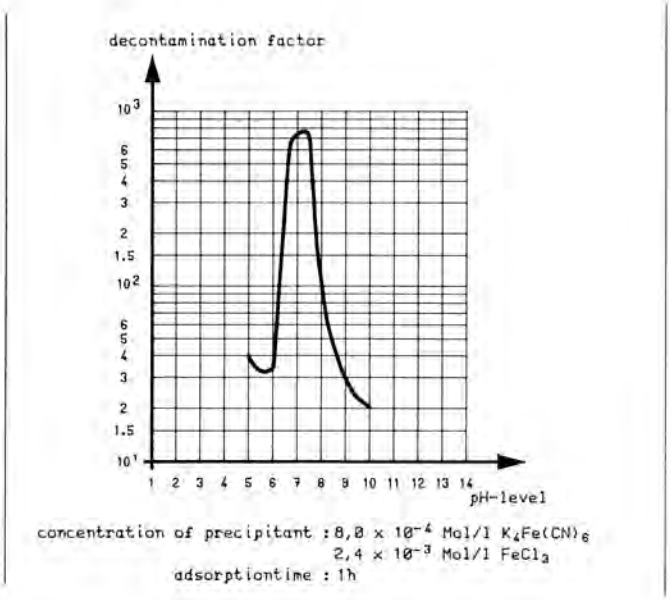

Fig. 2. Cs-decontamination with "Berlin Blue" (ferric ferrocyanide) as a function of pH-level of aqueous solution.

precipitation method. A total decontamination factor of 155 and a sum of the scale values of 0,6 was reached.

The technical practicability of the standard precipitation method from the aspect of automation, was confirmed by tests with non-radioactive solutions in a small 300 l pilot plant and in a larger 2000 l pilot plant.

The knowledge gained from these tests, which can be applied for the construction of this plant, is shown in Fig. 3.

Design and Construction of the Plant

BWB Engineering GmbH, Lörrach, was assigned with the task of the design and construction of a turnkey plant.

The task also consisted of integrating the newly developed precipitation process into the existing lay-out and was to fulfill the following demands:

1) The residue evaporator KKB I was to be replaced by the standard precipitation plant.

TABLE I

Test Results of Decontamination Tests With Radioactive Waste Water

Test solution			1	2	3	4	5	6
Analysis before precipitation								
γ - activity of waste water		Ci/m³	$7{,}3 \times 10^{-2}$	$8{,}2 \times 10^{-3}$	$3{,}6 \times 10^{-3}$	$4{,}5 \times 10^{-2}$	$7{,}5 \times 10^{-2}$	$1{,}7 \times 10^{-2}$
Proportion of nuclides	Mn 54	Ci/m³	–	–	–	–	$1{,}5 \times 10^{-3}$	$7{,}2 \times 10^{-5}$
	Co 58		–	$4{,}9 \times 10^{-4}$	$1{,}8 \times 10^{-4}$	–	$1{,}5 \times 10^{-2}$	$1{,}1 \times 10^{-3}$
	Co 60		–	$3{,}9 \times 10^{-3}$	$6{,}5 \times 10^{-4}$	$3{,}5 \times 10^{-3}$	$2{,}7 \times 10^{-2}$	$1{,}1 \times 10^{-4}$
	Ag 110 m		–	–	–	–	$2{,}5 \times 10^{-3}$	–
	Sb 125		–	–	–	–	$1{,}4 \times 10^{-3}$	
	J 131/133		–	–	–	–	–	$7{,}0 \times 10^{-3}$
	Cs 134		$2{,}0 \times 10^{-2}$	$3{,}3 \times 10^{-4}$	$5{,}4 \times 10^{-4}$	$1{,}8 \times 10^{-4}$	$7{,}5 \times 10^{-3}$	$3{,}7 \times 10^{-3}$
	Cs 137		$5{,}1 \times 10^{-2}$	$2{,}9 \times 10^{-3}$	$2{,}1 \times 10^{-3}$	$5{,}4 \times 10^{-4}$	$2{,}0 \times 10^{-2}$	$4{,}3 \times 10^{-3}$
	others		$2{,}2 \times 10^{-3}$	$5{,}7 \times 10^{-4}$	$1{,}8 \times 10^{-4}$	$1{,}7 \times 10^{-4}$	$1{,}2 \times 10^{-4}$	$7{,}2 \times 10^{-5}$
Content of boric acid	B	ppm	850	235	460	610	14000	600
Sum of scale values			210	24	10	6	120	130
Analysis after precipitation								
γ - activity of treated waste water		Ci/m³	$1{,}1 \times 10^{-4}$	$7{,}6 \times 10^{-5}$	$1{,}9 \times 10^{-5}$	$3{,}8 \times 10^{-5}$	$6{,}0 \times 10^{-4}$	$1{,}1 \times 10^{-4}$
Decontamination factor of individual nuclides	Mn 54	Ci/m³	–	–	–	–	1300	72
	Co 58		–	43	79	–	180	70
	Co 60		–	93	87	170	250	55
	Ag 110 m		–	–	–	–	8	–
	Sb 125		–	–	–	–	25	–
	J 131/133		–	–	–	–	–	280
	Cs 134		620	62	320	47	2000	140
	Cs 137		690	270	570	49	2200	185
	others		500	94	135	120	120	51
Sum of scale values			0,3	0,1	0,1	0,1	0,5	0,6
Total decontamination factor			660	110	190	120	125	155

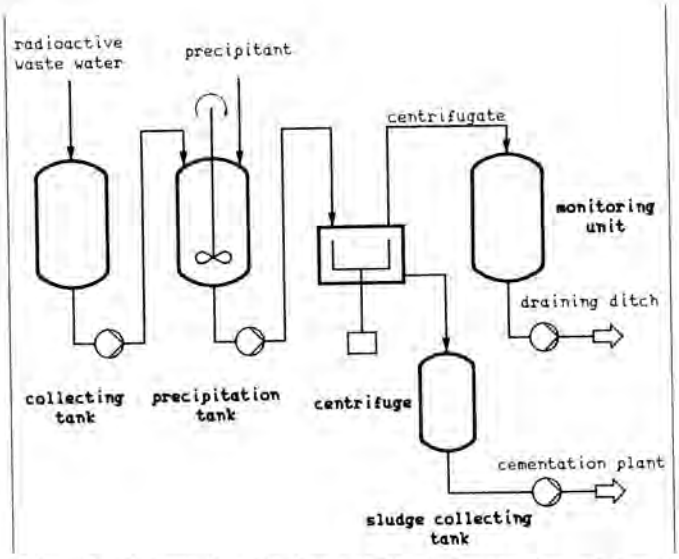

Fig. 3. Schematic display of Plant Separation of Precipitated Sludge by Centrifuge.

2) The residue evaporator KKB II had to be integrated into the system as standby especially for increased iodine activity.

3) Existing equipment, such as tanks, were to be integrated wherever possible into the new plant. (Fig. 4)

4) The standard precipitation plant had to be installed within the existing building.

5) The waste water treatment equipment was to be as versatile as possible enabling various methods of decontamination.

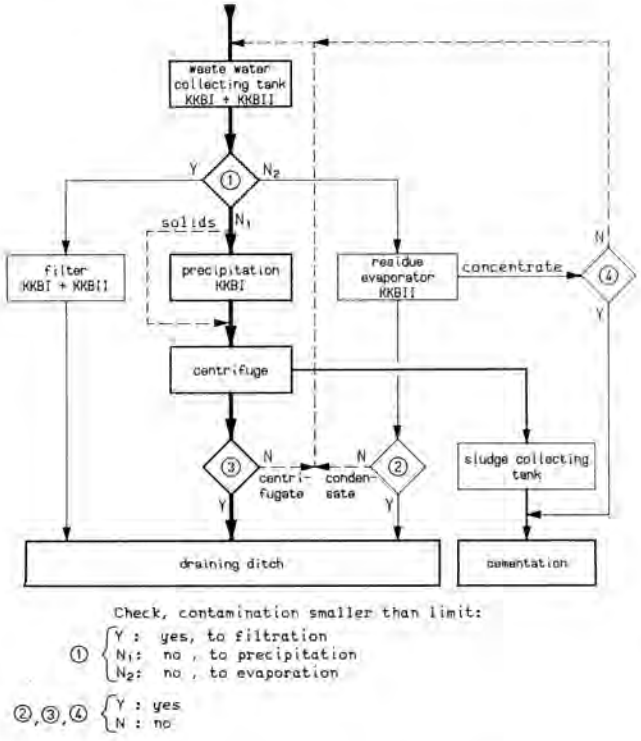

Fig. 4. Block diagram of the new plant.

After analyzing the contaminated waste water from KKB I and II and determining its texture, it is subjected to one of four different treatments, depending on its degree of contamination.

Filtration

Waste water that does not exceed the permissible radioactive contamination level is fed straight to the filter unit belonging to each block (KKB I and II) and then finally after passing through a monitoring unit, conveyed to the draining ditch. (Fig. 5)

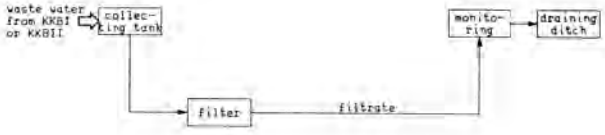

Fig. 5. Flow diagram filtration.

Centrifugation/Solidification

Waste water containing corrosion residue (magnetite) and other solids, which lead to an excessive contamination level, undergoes a separation treatment in a centrifuge.

Once the solids have been separated out, the clear liquid passes through the monitoring unit and into the draining ditch. The resulting sludge is collected and stirred into cement in the solidification box and finally filled into drums. (Fig. 6)

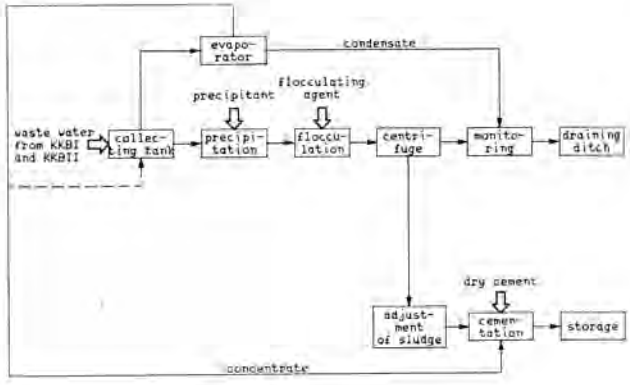

Fig. 6. Flow diagram centrifugation.

Precipitation, Flocculation, Centrifugation/ Solidification

Waste water that exceeds the permissible radioactive contamination level, due to radioactive components in solution, is subjected to chemical precipitation, flocculation and separation in a centrifuge. The clarified liquid passes through the monitoring unit into the draining ditch. The resulting sludge is collected and stirred into cement in a solidification box, from where it is filled into drums. (Fig. 7)

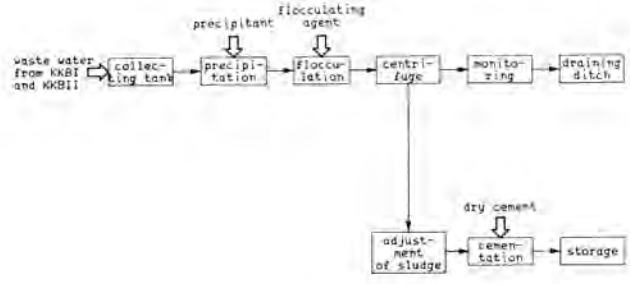

Fig. 7. Flow diagram precipitation.

Evaporation

In special cases, e.g. increased iodine activity, the waste water is fed into the existing residue evaporator installed in KKB II. The concentrate is collected and stirred into cement in a solidification box, from where it is filled into drums.

When the radioactivity is below the permissible contamination level, the condensate is fed into the draining ditch, but when it exceeds this level, it is fed to the precipitation unit via the collecting tanks. (Fig. 8)

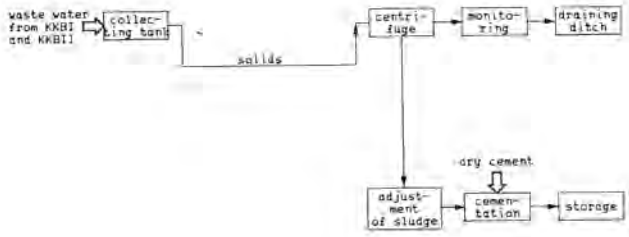

Fig. 8. Flow diagram evaporation.

BWB Engineering GmbH, Lörrach, set to work on this assignment, applied all the normal plant design procedures, observing the stringent regulations for protection against radiation, i.e.:

- process description
- marginal conditions
- design and construction schedule
- mass balance
- equipment calculations
- process flowsheets
- P & I diagrams
- layout
- piping drawings
- equipment procurement
- measurement and control design
- plant erection
- quality control
- commissioning
- testing
- plant documentation

Special Plant Components

The plant was furnished with the relevant components, such as vessels, pipes, pumps and valves, these having been tested and declared suitable for operation within nuclear power plants.

Special attention was given to the following components:

- centrifuges
- solidification plant
- measurement and control equipment

Centrifuges

The self-cleaning, centrifugal separators, used for this project, are especially suitable for liquids containing small solid particles. The extremely high centrifugal accelleration (approx. 6000 g) allows a separation of particles as small as 0,5 m.

The centrifuges work on the following principle: The material is fed via a central duct. Due to the difference in the density of the solid particles and the liquid, the heavy particles are transported to the wall of the rotating drum, where they are discharged at the furthest abaxial point. The liquid is discharged near the axis in the upper part of the centrifuge.

The centrifuge is fitted with guide plates to improve its efficiency.

Solidification Plant

The sludge, leaving the centrifuge, is collected in a tank, from where it is conveyed to the solidification plant. The solidification plant operates batchwise according to a method developed and licensed by the Nuclear Research Center in Karlsruhe, West Germany.

After determining the solid content and degree of radioactivity of the sludge in the sludge tank, drums (V=200 l) are filled with the corresponding amount of dry cement and fully automatically transported and coupled to the cementation box.

The drums are filled with the sludge in two steps:

Step 1: The drum is filled to the filling mark. The rotating indrum-mixer is gradually submerged into the sludge. When sludge and cement are homogeneously mixed, the mixer is pulled out again.

Step 2: The drum is filled again to the filling level and step 1 is repeated.

After the drums have been completely filled, they are automatically conveyed to the closing station, where they are closed, tested and prepared for storage. (Fig. 9)

This technology was specially developed by BWB Engineering GmbH, Lorrach, and has been successfully introduced in several nuclear power plants. The plant is installed within a totally shielded box and provided with automatic or remote control devices. All the essential components are installed redundantly.

Process Control

The operational concept provides for approx. 70 process steps, which are activated manually, but controlled by a microprocessor. This allows for a flexible operation of the plant, as requested by the client.

Samples are taken of crucial process streams. According to the laboratory analysis of these samples the corresponding programmed process step is then selected.

Anticipated Results and Improvements (2)

In the year 1977, 643 m^3 radioactive waste water was treated in evaporators in KKB I and II.

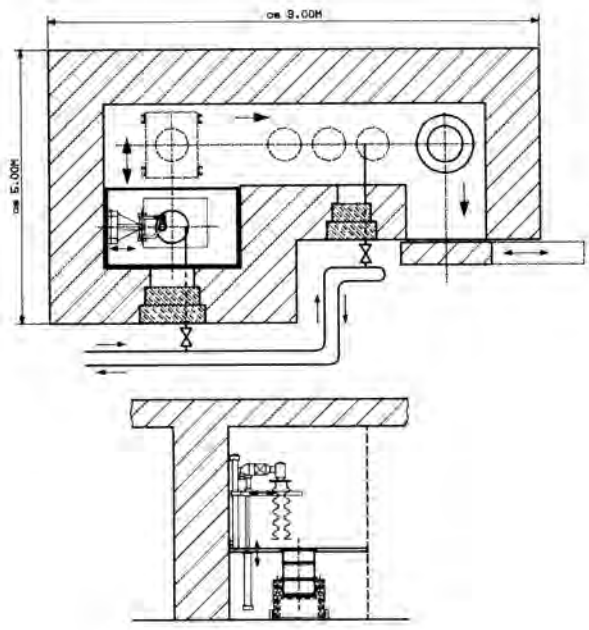

Fig. 9. Cementation plant conception.

The decontamination of radioactive waste water from PWR by means of chemical precipitation and centrifugation will have the following advantages over the evaporation method:

- volume reduction improved by a factor of 10, consequently less radioactive waste to be disposed of
- decontamination factor increased by a factor of up to 10, consequently lower radioactivity in the effluent
- operational problems with foaming eliminated
- reduced corrosion problems due to lower operating temperatures (max. 40°C)
- reduced space requirements
- reduced fixed capital investments
- reduced energy costs (under Swiss conditions these energy costs could be reduced from originally \$ 2/m^3 waste water to \$ 0,2/m^3 waste water)
- higher operating convenience due to higher degree of automation (process steps controlled by microprocessor.

Table II shows a comparison of the values reached by evaporation with the values anticipated with chemical precipitation followed by centrifugation according to pilot plant test results.

TABLE II

Comparison of Precipitation
Test Results With Evaporator

Waste water volume in 1977 KKBI + KKBII = 643 m^3 Content of boric acid (average): 550 ppm Activity : 10^{-3} to 10^{-1} Ci/m^3	Values reached by the installed evaporator	Values anticipated by precipitation and centrifugation, based on laboratory test
Activity of decontaminated waste water Ci/m^3	$5 \times 10^{-5} - 1 \times 10^{-4}$	$1 \times 10^{-5} - 1 \times 10^{-4}$
Decontamination factor	100	100 – 1000
Sum of scale values of decontaminated waste water	0.5 – 1	< 0.1 – 0.3
Volume reduction	41	400
Volume of concentrate from evaporator or centrifuge m^3	15.5	1.6
Activity in concentrate from evaporator or centrifuge Ci/m^3	0.1 – 10	1 – 40
Number of filled 200 l drums cemented	156	approx. 20
Dose rate at the surface of the filled 200 l drums mR/h	100 – 1000	some 1000

References

1. Krawczynski, S., B. Kanellakopulos, "The Removal of Radiocesium from Waste by Precipitation by Means of Heavy-Metal Salts of the Ferrocyanide", Atomenergie, 6. Ig. (1961) Nr. 5.

2. Bucher, T., "The Treatment of Radioactive Waste Water by Means of Chemical Precipitation and Centrifugation in Nuclear Power Station, Beznau", VGB Kernwerkstechnik 61, Heft 8.