

INDUSTRIAL SCALE REMOVAL OF CESIUM WITH HEXACYANOFERRATE EXCHANGER- PROCESS REALIZATION AND TEST RUN

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ABSTRACT

At the Loviisa NPS all liquid waste, i.e. spent resins and evaporator concentrates, has been stored in a large tank storage facility. Dominating radionuclides in the evaporator concentrates have been Cs-134 and Cs-137. By removing cesium from the waste, purified liquid can be released within licensed release limits, and cobalt as a second dominating nuclide is left in a small waste volume on the bottom of the tank. Since 1985 use of inorganic hexacyanoferrate-based materials for purification of cesium has been studied. A full-scale system for cesium removal, called IVO-CsTreat System, was constructed in 1990-91. A method to produce the ion exchanger in granular form in industrial scale was developed and the facility to produce it was constructed. The ion exchange material was produced in 1991 and the full scale purification facility was commissioned at the Loviisa NPS in October 1991. In the test run, 253 m³ of concentrate was purified between 31 October 1991 and 11 June 1992 with three ion exchange columns, each with volume of 8 liters. Volume reduction factor of over 10 000 was achieved as a ratio of liquid and ion exchanger volume. Decontamination factor for cesium was about 2 000.

INTRODUCTION

At the Loviisa NPS (2 x 465 MWe, VVER-type) the unit 1 was commissioned in 1977 and the unit 2 in 1980. Ever since the beginning of the operation all liquid waste, i.e. spent resins and evaporator concentrates, has been stored in a large tank storage facility. By the end of 1991 545 m³ of evaporator concentrates and about 183 m³ of spent resins were stored in the tanks.

All the time the aim of the plant has been to minimize the waste volume. The practice in waste management and content of the research work has been reported.(1,2) Volume reduction of evaporator concentrates has been the topic with first priority.

Close to 50% of the content of radionuclides in the evaporator concentrates consisted of Cs-134 and Cs-137. In the tank TW10B01 even close to 75% of total activity and over 99% of total solution activity was of cesium. By removing cesium from this tank, purified liquid can be released within licensed release limits, and cobalt as a second dominating nuclide is left in a small waste volume on the bottom of the tank.

Since 1985 use of inorganic hexacyanoferrate-based materials for purification of cesium has been studied. After laboratory and pilot plant tests a full-scale system for cesium removal, called IVO-CsTreat System, was constructed. By the same time the method to produce hexacyanoferrate in granular form in industrial scale was developed and the facility to produce it was constructed. The ion exchange material was produced in 1991 and the full scale purification facility was commissioned at the Loviisa NPS on 31 October 1991.

INTERIM STORAGE OF EVAPORATOR CONCENTRATES

The Loviisa NPS is equipped with a large tank storage facility for liquid waste. The facility includes totally eight stainless steel tanks, with a capacity of 300 m³ each. Four of the tanks are used for storage of evaporator concentrates, three tanks for spent resins, and one tank is kept in reserve.

Evaporator concentrates are collected into the tanks of interim storage facility. Due to natural decay the amount of short lived nuclides decreases considerably during the storage period. Most nuclides are settled onto the bottom of the tank.

Annually, some 100 m³ of concentrates, including some 20 GBq of corrosion and fission products and some 10 TBq of tritium, have been released from the surface of the tank into the sea. These releases correspond to 2 per cent and 6 per cent, respectively, of the annual release limits.(1) Table I shows the amounts of evaporator concentrates accumulated and released at the Loviisa NPS. On 31 December 1992 the storage tanks contained the accumulation of 486 m³ of concentrates, which was about 41 per cent of the storage capacity.

NUCLIDE CONTENT OF THE CONCENTRATES

Evaporator concentrates contain a variety of elements including measurable amounts of cesium, cobalt, nickel, silver, manganese and antimony. Total amount of radionuclides is shown in Table II.

Cesium content of the tank TW10B01 was purified in a test run. On 31 October 1991, when the test run was about to start, this tank contained 18.5 GBq of Co-60, 3.9 GBq of Cs-134 and 68.7 GBq of Cs-137.

TABLE I
Amounts of Evaporator Concentrates Accumulated and Released in the Loviisa NPS

Year	Accumul (m ³)	Released (M ³)	Stored 31.Dec (m ³)
1977	311	-	311
1978	204	300	215
1979	116	295	36
1980	184	155	75
1981	175	69	181
1982	223	55	349
1983	120	81	388
1984	170	82	476
1985	114	116	474
1986	51	102	423
1987	50	92	381
1988	55	72	364
1989	174	82	456
1990	185	124	517
1991	115	90	542
1992			486

TABLE II
Accumulated Activity of Evaporator Concentrates

Year	Released GBq	31 Dec. GBq
1978	17.8	4
1979	15.1	31
1980	17.9	85
1981	2.7	636
1982	13.4	429
1983	22.2	350
1984	20.5	359
1985	17.8	290
1986	16.9	269
1987	13.0	227
1988	15.0	201
1989	21.0	177
1990	18.0	213
1991	3.0	189
1992		239

Concentration profile was measured for each tank, TW10B01, TW10B02, TW10B03, and TW10B04, as a function of height from the tank bottom (Fig. 1). As can be seen, cesium is uniformly distributed along the tank, but cobalt is mainly below the lowest 10 cm.

In the evaporator concentrates there appear also other nuclides than cesium and cobalt. When concentrates are collected, there are normally some measurable amounts of Mn-54, Ag-110m and Sb-124. These nuclides with half lives of 312 days, 260 days and 60 days, respectively, will considerably decay during the storing period of some years. Also these nuclides will mostly settle down towards the tank bottom.

Totally the concentrations of radionuclides are very low in the concentrates of the Loviisa NPS. As the fuel rods are very clean and tight, only small amounts of fission products appear in waste. Low concentration of corrosion products is a result of good materials and good operation practice.

PRINCIPLES OF CESIUM SEPARATION

In the construction of the cesium separation system, IVO-CsTreat System, the available systems were utilized as far as possible. Tanks, pipelines and pumping system were available in such a form that they could be modified for this system.

The purification system consists of the following steps:

- pH adjustment of the solution,
- pumping of the solution via a feed tank into the purification unit.

The purification unit includes the following steps:

- prefiltering of solid fines greater than 0.1 m,
- ion exchange of cesium with specific material in the columns,
- monitoring of cesium breakthrough,
- control of pressures over the filters and columns.

Figure 2 shows the simplified flow-sheet of the process.

pH of the solution is adjusted in the existing storage tanks. In the tank TW10B01 pH was 13.7 before the treatment. It was lowered to 11.5 by pumping 60% nitric acid into the storage tank. In order to make this possible, pipelines were installed for inlet of acid. The system for removal of gases existed in the storage facility.

After pH adjustment the solution is kept isolated for some weeks before the purification is started. During this time most particulate matter is settled onto the bottom. When the purification is started, concentration profile of radioactive nuclides is similar to the original (Fig. 1).

A special system was constructed for pumping the solution. Because settled material on the bottom of the tank must not be disturbed, solution is pumped from the surface.

The existing 5 m³ tank of the Monte-Jus system was modified to be used as a feed tank of the system.

The purification unit was constructed into an existing room with a floor area of about 20 m². The system can be constructed even to a smaller area, if needed. Figure 3 shows the layout of the system at the Loviisa NPS.

In the purification unit the solution is pumped with controllable pump for purification with the specific ion exchanger. Pressures over the filters and columns are controlled with local indicators. Breakthrough of cesium is controlled with an online single channel analyzer.

In the purification unit there are two locations for ion exchange columns. The system can be operated either with one column or with two columns in series. In the test run the option with two columns in series could not be fully tested, because the full-scale system operated much better than was anticipated after the pilot plant tests.

The ion exchange material is packed in stainless steel columns (Fig. 4). Their volume is 8 litres of ion exchange material. The column is 60 cm in length and 14 cm in diameter. It was planned to be ideally disposed of in the same type of concrete container as will be used for solidification of other liquid waste. Naturally, the shape and size of the columns can be modified, if there will be requirements for other type of disposal container.

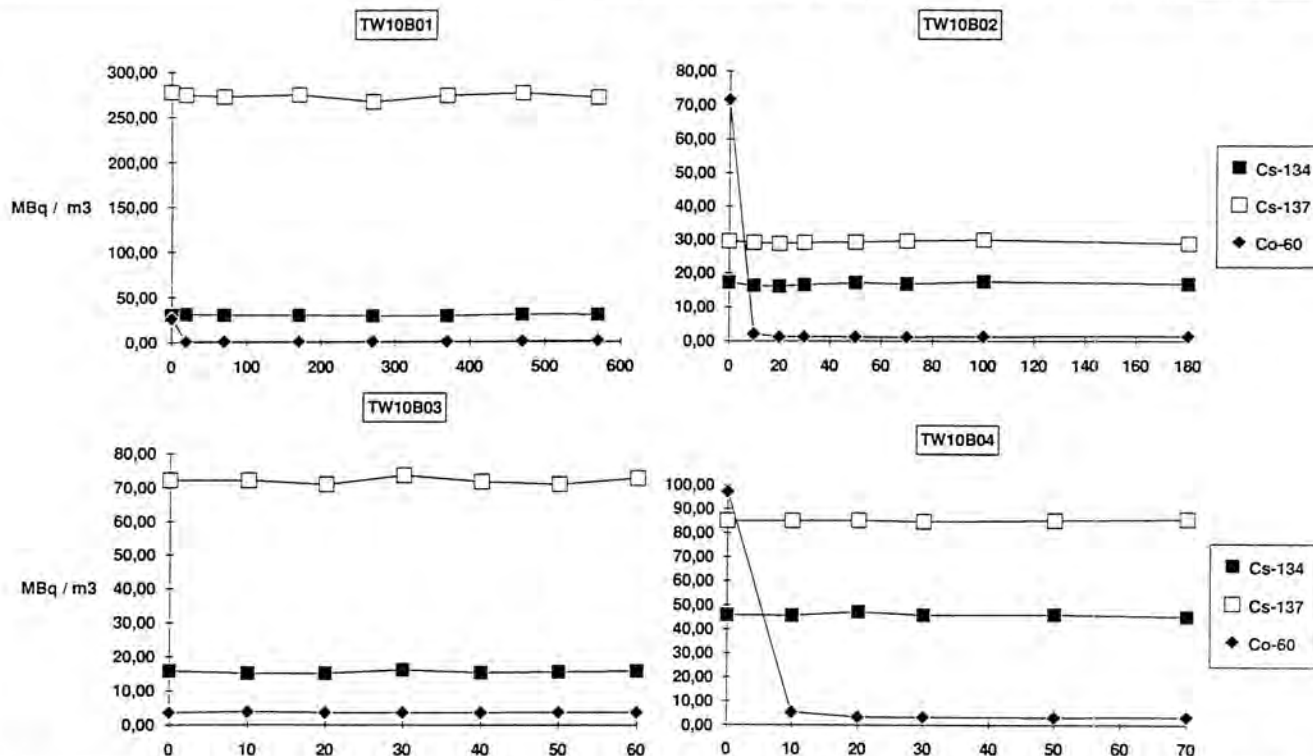


Fig. 1. Concentration profile of Cs-134, Cs-137 and Co-60 in the tanks TW10B01 - B04 as a function of height from the tank bottom.

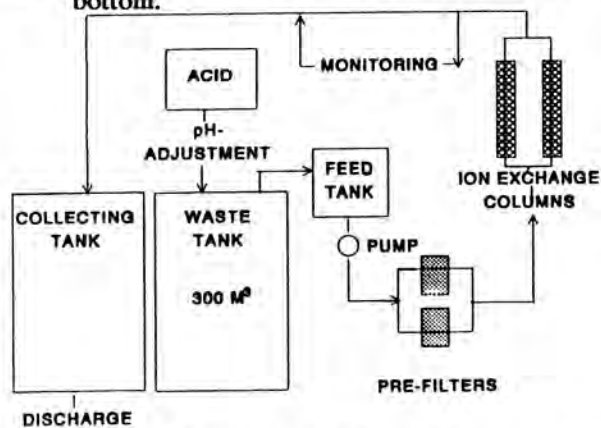


Fig. 2. Simplified flow-sheet of the IVO-CsTreat system.



Fig. 4. Cesium selective ion exchange material is used in stainless steel columns with volume of 8 liters.

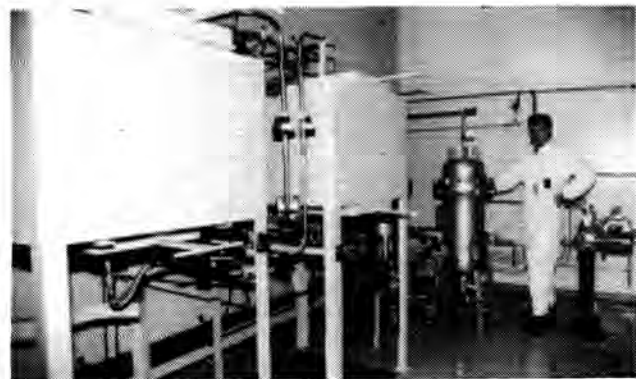


Fig. 3. IVO-CsTreat system installed at the Loviisa NPS.

TEST RUN WITH THE FULL SCALE SYSTEM

In the test run, 253 m³ of concentrate was purified between 31 October 1991 and 11 June 1992 with three ion exchange columns, with volume of 8 liters each.

The concentrate had a total salt content of about 240 g/L, including over 40 g/L of boron, 60 g/L of sodium, and 10 g/L of potassium.

In the beginning of the test run only one column was used. The performance of the system with one column appeared to be extremely good. 1% breakthrough of cesium was observed at 24,500 bed volumes. In the laboratory tests 1% breakthrough occurred at 2,800 bed volumes, and in the pilot plant tests it occurred at 11,500 bed volumes.

The second column was taken into use when 0.3% breakthrough occurred in the first one at 22,800 bed volume (182 m³). The first column was removed from the system when about 210 m³ was pumped through this column, and the

operation was continued with the second column. Only about 53 m³ was pumped through the second column before it was taken out of use.

With the third column only about 17 m³ was purified before the test run was stopped. It is expected that a remarkable amount of ion exchange capacity is still available in this third column, and it will be utilized in the purification of the next tank.

When the solution was purified, total decontamination factor of over 2,000 was achieved. When the original solution consisted some 3×10^5 Bq/L of cesium, in the purified solution there was in average less than 150 Bq/L of cesium. In addition to this there was a small fraction of cobalt, which is not settled onto the tank bottom nor was captured by the pre-filters. Some 1 kBq/L was released with purified liquid, corresponding to slightly over 1% of the original cobalt inventory.

The performances of the second and third column were much poorer than of the first column. This was caused by an unexpected increase in pH when about 180 m³ of solution was treated. From this experience it appeared that close control of mixing in pH control and continuous pH monitoring is essential.

By the end of 1992, the remaining sludge from the tank TW10B01 was pumped into the tank TW10B02.

Second tank TW10B02 will go for purification in the beginning of 1993.

When the ion exchange column is exhausted, it is taken out of use and is transported and placed into a storage and final disposal container. Good experience from this changing and transport work was gained. Figure 5 shows the phase when transport container for columns is in its place to receive the column from the purification unit. Figure 6 shows the container into which 12 columns can be placed for storage and final disposal.

FINAL DISPOSAL OF THE ION EXCHANGE MATERIAL

All low and intermediate level waste from the Loviisa NPS will be disposed of at the power plant site. (3) Solidified wastes will be disposed of in concrete containers having diameter of 1.3 m and height of 1.3 m, and with inner volume of 1 m³ and outer volume of about 1.7 m³.

A final disposal container for spent cesium removal columns has the same outer dimensions as a container for solidified waste (Fig. 6). Spent ion exchange columns will be disposed of in a concrete container having 12 disposal holes.



Fig. 5. Ion exchange column is changed from the IVO-CsTreat System's purification unit.

All waste solidified in concrete containers will be disposed of in a rock vault. 7,400 m³ of solidified waste was initially planned to be disposed of in a vault with volume of 30,000 m³. (3) Cesium separation and release of purified liquid will reduce the volume of this rock vault.

Disposal of spent columns in the manner described above will improve the safety of final disposal compared to direct cement solidification of concentrates. In the direct cementation product there is a 10 cm layer of inactive concrete between the active concrete and the surface of the container. In the container for spent columns from the cesium separation system, the layer between the columns and the container surface is 30 cm. The stainless steel wall of the column, 3 mm thick, works also as an effective barrier against release of activity into groundwater. In addition, leachability of cesium from the exchanger into groundwater is very low. (4)

ECONOMICAL RESULTS

An alternative treatment for cesium removal and release of purified liquid is direct solidification of concentrates with cement, presuming that release without treatment is not possible. Economical savings come both from reduction of solidification need and from reduction of room volume in final repository.

If evaporator concentrates are solidified with cement, about 1.9 m³ of solid material is formed from each m³ of solution. When the volume of concrete package is taken into account, 1 m³ of concentrates produces 3.3 m³ of final product into the repository.

As an average in the test run, 10,000 liters of evaporator concentrates were purified with one liter of ion exchanger, or one column purified 80 m³ of concentrates. Thus, one concrete container can contain cesium from 960 m³ of concentrates.

If 960 m³ of concentrate is cemented, there will be 3168 m³ of final product in the repository. Compared to the outer volume of 1.7 m³ of one concrete container for spent columns, there is a volume reduction factor of over 1800.

When a small amount of liquid has to be solidified from the bottom of the tank, final volume reduction factor will be somewhat smaller. In the case of the test run, about 3 m³ of slurry was on the bottom of the tank TW10B01 waiting for later solidification. Taking into account about 10 m³ of solid product coming from this slurry, final volume reduction factor for the test run was about 80, when calculated from the reduction of final disposal volume in the repository.

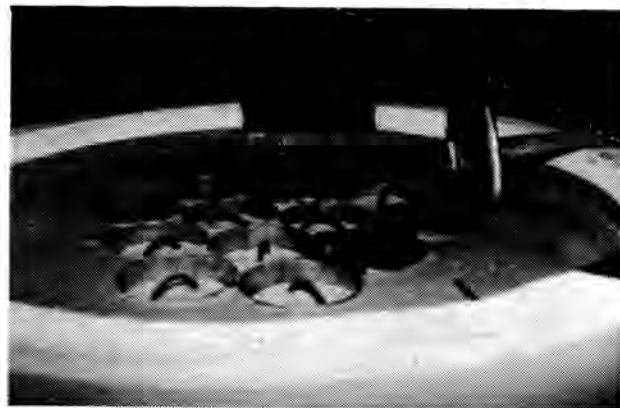


Fig. 6. Spent ion exchange columns are placed into a concrete container for storage and final disposal.

If, later on with better pH control, the system gives the same performance as was found with the first column, remarkably better savings are available. If 180 m³ of concentrates are purified with a single column, volume reduction factor in final repository is about 3,000. Taking into account the slurry from the tank bottom, final volume reduction factor is again over 80. Thus, the amount of slurry has a great effect on the final volume reduction factor.

Some 7000 USD can be saved as operation costs of the cement solidification plant, if one cubic meter of concentrates can be eliminated. In addition to this, over 1000 USD can be saved in final disposal. The savings which were calculated for the test run were totally over USD 2 millions. Compared to the investment costs of some USD 0.6 million and operation costs of USD 0.1 million, the system appeared to be a good investment.

SUMMARY

Very selective system was developed for removal of cesium from evaporator concentrates with high salt content. Based on this work an industrial scale cesium removal system, called IVO-CsTreat System, was developed and constructed at the Loviisa NPS. A test run of the system took place from October 1991 to June 1992. 253 m³ of evaporator concentrates were purified with 24 litres of selective ion exchange material. The performance of the system exceeded the results of the laboratory and pilot scale tests. The system appeared to be very cost effective. In the test run volume reduction factor as

a ratio of treated liquid and volume of ion exchanger was over 10,000. In final repository, when the volume of packed ion exchange columns is compared to the volume of cemented concentrate, the volume reduction factor is about 1,800, and still about 80 when the treatment of slurry from the tank bottom is taken into consideration.

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