Analysis of Hot Cell Paint

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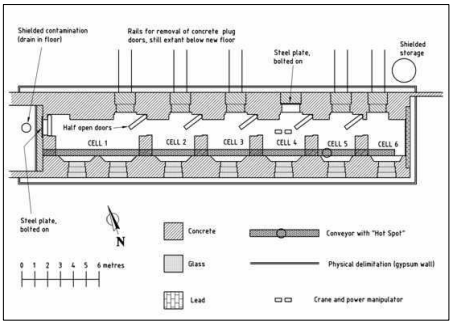
Introduction

The decommissioning of the nuclear facilities at Risoe, Denmark, involves decontamination of 6 hot cells. During operation from 1964 to1989 the hot cells were used for examination of spent fuel elements and production of irradiated cobalt pellets. Thus the cells are contaminated with actinides, fission products and some activation products. The interior compartments of the concrete construction are sealed with a steel liner, which is coated with epoxy paint. The paint contains significant levels of PCB's and lead. The decontamination will be done by sandblasting the paint off the steel liner.

We expect to get app. 100 barrels, or 10,000 liters, of sandblasting material mixed with contaminated paint particles. A subsample is collected from each barrel, which is going to be analyzed to estimate the total inventory of the radionuclides.

The challenge is to establish a method for analyzing the alpha emitting radionuclides. For this purpose, the material has to be fully dissolved to release the radionuclides to a solution from the matrix. Some preliminary testing has been performed, and it was found that the epoxy paint cannot be decomposed by conventional methods, e.g. acid digestion using aqua regia and ashing at less than 1000 ℃ . Leaching of the material using boiling aqua regia may however liberate virtually all actinides adsorbed. Due to the relatively high concentrations direct alpha spectrometry and low energy gamma and X-ray spectrometry can be used both to provide approximate concentrations of Pu-isotopes and to verify the amount of Pu and Am removed from the surface during leaching.



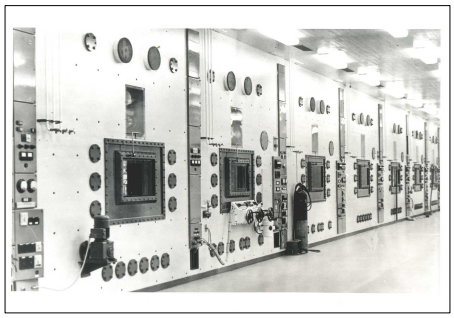


Fig. 1 Overview (top) and historical photo of the cells taken from the front area (bottom). One of the cells is a double cell.

Decontamination method for the hot cell

The paint "Amercoat 74" was to be a strongly cross-linked catalyzed epoxy coating with exceptional resistance to alkalies and organic solvents and with excellent radiation resistance and thus easily decontaminated. Analyses have shown considerable amounts of lead and PCB's in the paint, which makes it difficult to decompose and problematic in the analysis of Pu isotopes by ICP-MS.

From 1990 to 1994 decontamination of the surfaces in two of the cells was tested by using high pressure water jetting, but the result was very poor. It is now decided that the paint on all inner surfaces will be blasted off using corundum. Corundum has been chosen instead of sand because it produces fewer airborne particles while blasting.

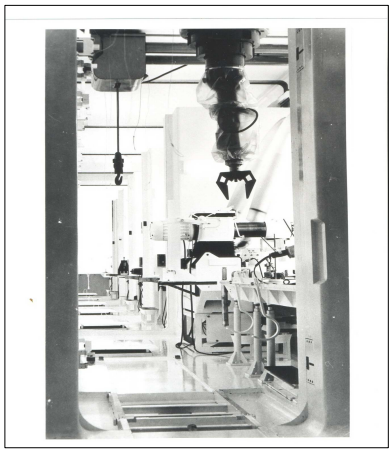


Fig.2 Historical photos from inside hotcells before they went into operation

The blast nozzle will be controlled using a robot arm mounted in the openings previously used for the master-slave arms. The mixture of contaminated paint and corundum is sucked into flexible tubes and transferred to barrels. The decontamination will reduce the dose levels in the cells, and makes personnel entrance possible for final cleanup. For estimate the inventory of alpha and beta emitters, a radiochemical analysis has to be carried out before decontamination.

Experiment and Methods

Sampling

Seven paint samples were scraped from the inside surface of one plug from each cell (two from cell 1) using a knife and collected in plastic bags for analysis. Due to low activity, the sample from cell 6 was only analysed for alpha emitters.

Homogeneity analysis

Four subsamples were taken from each sample except for cell 5, where 2 subsamples were taken. The samples were measured by low-energy HPGe detector for ^{137}Cs and ^{241}Am to evaluate the homogeneity of radionuclides on each paint sample.

Leaching the radionuclides from the paint

One subsample from each sample was taken to a beaker, *aqua regia* (HCl+HNO_3) was added to the beaker, and the beaker was covered by a watch glass. The sample with solution was heated at 200℃ for 5 hours. After cooling, the solution was filtered through a glass fibre filter and the filter was washed with 6M HCl, the washes were combined with the filtrate, which was used for radiochemical analysis of plutonium isotopes, ^{241}Am and ^{243,244}Cm. The filters were measured by HPGe detector to estimate the leaching rate of ^{137}Cs and ^{241}Am.

Radiochemical analysis for plutonium isotopes, ^{241}Am and ^{90}Sr

Fig. 3 shows the radiochemical separation procedure for separation of Pu, ^{241}Am, and ^{243,244}Cm from the acid leachate using Risø procedure (Chen et al. 2001; 2002). ^{242}Pu and ^{243}Am were used as chemical yield tracers. The ^{241}Pu, ^{242}Pu and ^{243}Am in the samples were determined in another fraction without addition of tracers. ^{238}Pu, ^{239,240}Pu, ^{241}Am, and ^{243,244}Cm were measured by alpha spectrometry, ^{239}Pu, ^{240}Pu, ^{242}Pu were measured using ICP-MS, and ^{241}Pu was measured by LSC.

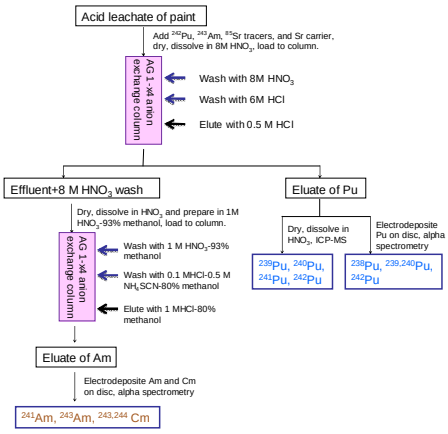


Fig.3 Radiochemical analytical procedure for isotopes of Pu, ^{241}Am and ^{243,244}Cm

Results and Discussion

Table 1 shows the distribution and homogeneity of radionuclides in the paint. High ^{137}Cs and ^{241}Am concentrations were observed in the paint from Cells 1-3, but much lower in Cells 4-5. The distribution of radionuclides in the paint from the same sample is very much inhomogeneous. In addition, the ratio of ^{137}Cs/^{241}Am in the different samples are also different, indicating different sources.

Table 2 shows the leaching rate of radionuclides As high as 95-99% of ^{241}Am was leached out from the paint by *aqua regia*, while a slightly low leaching rate of 78-99% was observed for ^{137}Cs. By repeated leaching using HNO_3 and HCl, the leaching rates of Am and ^{137}Cs have been improved to 97-99% and 94-99%, respectively.

Table 3 shows the concentrations of Pu isotopes, ^{241}Am and ^{243,244}Cm in the paint, a similar trend was observed as for ^{137}Cs in Table 1 - much higher activities were observed in Cell 1-3, and the lowest in Cell 6. The isotope activity ratios of ^{240}Pu/^{239}Pu and ^{238}Pu/$^{239+240}$Pu are relatively high, and range between 0.5-1.7 and 0.3-1.7, respectively, indicating their reprocessing source. ^{242}Pu and ^{243,244}Cm were also measured in these paint samples, ratios of ^{242}Pu/^{239,240}Pu and ^{243,244}Cm/^{241}Am vary between (0.48-1.64)×10^{-3} and 0.06-0.16, respectively, indicating a high and variable burnup of the fuel. The activity ratios of ^{241}Am/^{241}Pu in all 7 samples are close to be 0.092-0.136. The age of the sample can be estimated to be 25-35 years if we suppose all ^{241}Am in the samples comes from the decay of ^{241}Pu without significant loss. This value is in line with the operation period of the facility from 1964-1989.

Table 1 Distribution and homogeneity of ^{137}Cs and ^{241}Am in 6 paint samples from 5 cells (Analytical uncertainty < 5%)

Sample ID	Weight, mg	^{137}Cs, cps/g	^{241}Am, csp/g	^{137}Cs/^{241}m
1A	29-45	653-1540	72-222	8.3-9.1
1B	28-40	23100-32700	1900-2800	10.8-11.6
2	9-22	53600-107000	7700-16500	6.5-6.9
3	19-33	12800-15800	2580-3340	4.4-5.0
4	56-119	176-431	16-44	6.9-11.3
5	130-150	291-342	8-12	29-37

Table 2 Leaching rates of ^{137}Cs and ^{241}Am in 6 paint samples from 5 cells by *aqua regia (analytical uncertainty <5%)*

Sample ID	Weight, mg	Leaching rate, %	
		^{137}Cs	^{241}Am
1A	29.5	7.89	1.29
1B	39.1	4.73	0.90
2	9.2	1.18	0.76
3	19.5	2.20	1.25
4	85.7	21.19	2.52
5	130.3	8.99	5.01

Table 3 Distribution of Pu isotopes,^{241}Am, and ^{90}Sr in 7 paint samples from 6 cells by radiochemical analysis, Bq/g (analytical uncertainty <5%)

Sample	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu	^{241}Am	^{243,244}Cm	^{238}Pu/$^{239+240}$Pu	^{242}Pu/$^{239+240}$Pu	^{239}Pu/^{240}Pu	^{241}Am/^{241}Pu	^{243,244}Cm/^{241}Am
1A	341	233	228	6898	0.48	809	63	0.741	1.04x10^{-3}	1.02	0.117	0.078
1B	11670	4937	4899	136500	11.5	17910	2657	1.19	1.17x10^{-3}	1.01	0.131	0.148
2	96314	20458	34986	1194000	89.8	158000	23670	1.74	1.62x10^{-3}	0.585	0.132	0.150
3	17955	3626	6787	233700	16.5	318400	4556	1.72	1.59x10^{-3}	0.534	0.136	0.143
4	79	23	37	1108	0.068	145	11	1.32	1.14x10^{-3}	0.619	0.131	0.079
5	48	98	56	1017	0.074	107	6.9	0.310	0.48x10^{-3}	1.76	0.105	0.064
6	4,6	1.6	2.0	82	0.006	7.6	1.2	1.27	1.64x10^{-3}	0.842	0.092	0.157

References:

Chen, Q.J.; Aarkrog, A.; Nielsen, S.P.; et al. Procedures for determination of ^{238,239,240}Pu, ^{241}Am, ^{237}Np, ^{234,238}U, ^{228,230,232}Th, ^{99}Tc and ^{210}Pb-^{210}Po in environmental materials. Risø National Lab., RISØ-R--1263(EN), 2001.

Chen Q.J.; Hou X.L., Nielsen S.P. et al. Separation of Sr from Ca, Ba and Ra in the determination of radiostrontium by means of simple precipitation using $Ca(OH)_2$, $Ba(Ra)Cl_2$ or $Ba(Ra)SO_4$. *Anal. Chim. Actc*, 466 (1): 109-116, 2002.