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Analysis and Selective Treatment of Radioactive Waste Waters and Sludges

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1. Introduction

In the Hungarian PWR-type nuclear power plant Paks (four 500 MW_e capacity VVER-440/213 blocks) the radioactive waste waters are collected in common tanks. These water streams contain radioactive isotopes in ultra-low concentration and inactive compounds as major components (borate 1.7 g/dm^3, sodium-nitrate 0.4 g/dm^3, sodium-hydroxide 0.16 g/dm^3, and oxalate 0.25 g/dm^3).

Up to the present the low salinity solutions were evaporated (by adding sodium-hydroxide) till 400 g/dm^3 salt content (**pH~13**) and after solidification by cementing buried. There is about 6000 m^3 concentrated evaporator bottom residue in the tanks of the PWR. In order to separate the inactive salt content before cementing a Liquid Wastewater Treatment Technology (LWT see Figure 1.) was developed to treat this wastewater before solidification and burial (Pátzay et al., 2006).

The long-life radionuclides are present in very low concentration (10^{-9}-10^{-12} mol/dm^3) as ions, suspended, colloid particles and in complex (EDTA, oxalate, citrate) form. In this technology the SELION CsTreat cesium selective ion exchanger is used for the selectice separation of radiocesium isotopes (^{134}Cs, ^{137}Cs). The SELION **CsTreat** cyanoferrate based cesium-selective ion exchanger is not stable at pH>11 (see reaction equation below), so the use of CsTreat needs partial neutralisation of the evaporator bottom residue to pH~9-11, and during neutralisation sodium-borate crystals precipitate with about 15-30% of the radioactivity.

$$K_2Co[Fe(CN)_6] + 2OH^- \Rightarrow 2K^+ + [Fe(CN)_6]^{4-} + Co(OH)_2 \qquad (1)$$

The contaminated crystals should be washed to remove the radioactive isotopes from the crystals. To eliminate the generation of radioactive borate crystals and additional wastes we have developed a $M_2Ni[Fe(CN)_6]$ type cesium selective granulated ion exchanger (where M is an alkali ion) which has good stability even at pH>11.

Based on this new cesium selective ion exchanger stable at pH>11 we have modified the radioactive evaporator bottom residue treatment technology at the nuclear power plant. The basic idea of the new technological scheme is the selective separation of all radionuclides with inorganic sorbent materials or reagents in very simple processes without any prior neutralization, dilution. After the separation of all radionuclides the inorganic salt content
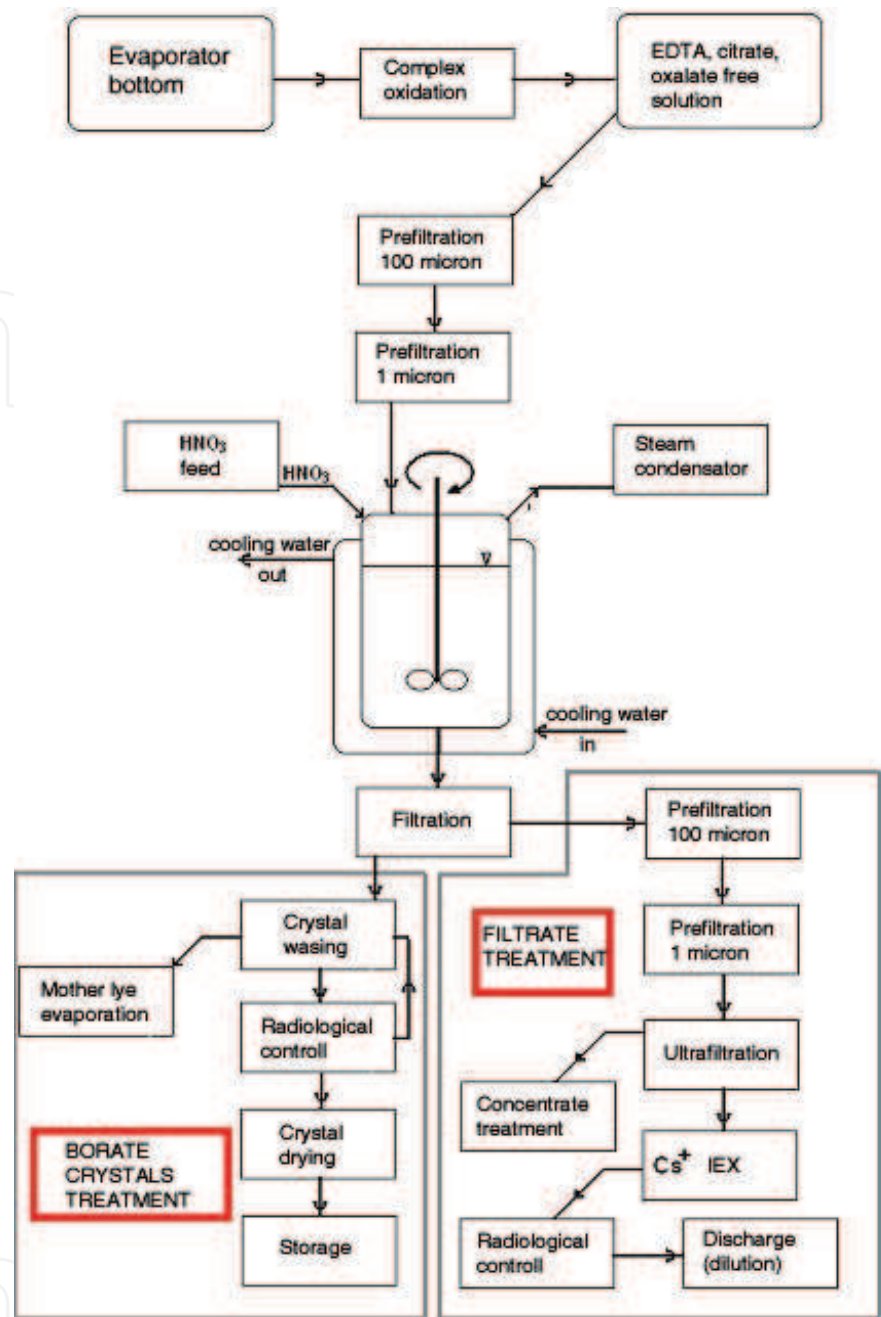
Fig. 1. *The Liquid Wastewater Treatment Technology*

(borates, partially nitrates) could be separated with crystallization using nitric acid neutralization and the inactive crystals could be treated as chemical waste. In the first part of this report this modified separation technology will be discussed.

In the Nuclear Power Plant Paks at the bottom of some radioactive liquid waste containing tanks there are segregated sludge phases, containing more or less organic complex builder compounds (including EDTA, citrate and oxalate compounds). The radioactive waste water treatment technology, developed at the plant is not suitable to treat sludges, so a modified technology is needed using cementing as solidification. For this technology the detailed analysis of these sludge phases are of great importance. According to this problems we started a research work to investigate the international experience in the analysis of

radioactive sludges and fulfilled laboratory scale experiments for chemical and radiochemical analysis of different sludge samples. In the second part of this report the analysis of these radioactive sludges will be discussed.

2. The modified liquid wastewater treatment technology

The developed modified technology consists of the following parts:

- Firstly the high salt content, strongly alkaline (*pH*~13-14) evaporator bottom residue is **microfiltered**.
- Then the free EDTA, citrate, oxalate content is **oxidized** with underwater plasma torch and with Fenton oxidation (in this process Co isotopes removed by precipitation as oxide-hydroxide and can be separated by filtration). The treated solution is microfiltered and ultrafiltered.
- Selective separation of the radioactive cesium isotopes (^{137}Cs, ^{134}Cs) using ion exchange material stable at alkaline pH.
- Crystallization of borates from the mother lye by neutralization with nitric acid.

The modified waste treatment technology was tested at the NPP. After microfiltration about 500 dm^3 evaporator bottom residue was oxidized with underwater plasma torch for the EDTA, citrate and oxalate removal. The oxidized evaporator bottom residue was then microfiltered and ultrafiltered to remove suspended matter and cobalt precipitation from the solution having a pH~12.3 The separation efficiency of the ultrafiltration is shown in Table 1.

	^{60}Co activity concentration (Bq/kg)	%	^{134}Cs activity concentration (Bq/kg)	%	^{137}Cs activity concentration (Bq/kg)	%
Feed	2310	100	1350	100	181000	100
Permeate	258	11.2	1210	89.6	164000	90.6

Table 1. *Ultrafiltration of the waste water after oxidation of the complex compounds*
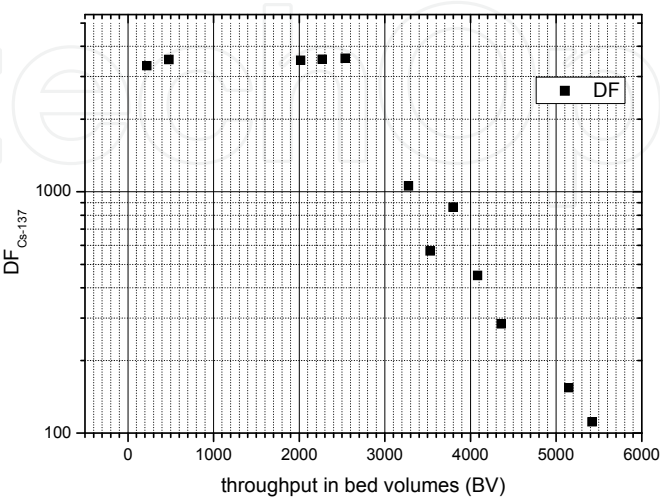

Fig. 2. *Breakthrough curve of ^{137}Cs (BV-bed volume)*

The solution purified from radioactíve cesium was then acidified with concentrated nitric acid in 20 dm³ batches in a cooled mixed reactor till pH~9.0. The crystallization reactor is shown in Figure 3.
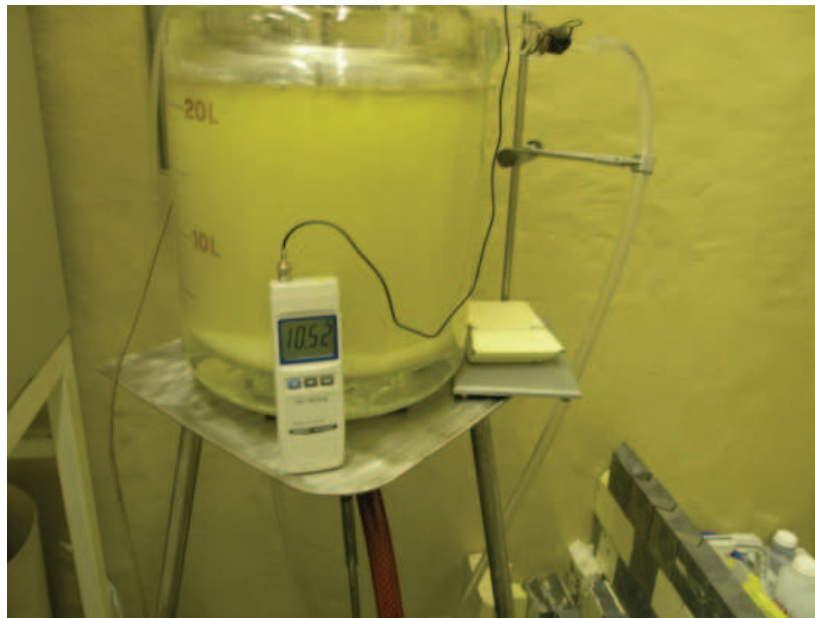

Fig. 3. *The crystallyzation reactor*

Fig. 4. *The separated wet crystals by the original (left) and by the modified (right) technology*

The crystals were separated by filtration, dried at 50 ^{0}C and weighted. The crystalline product contained mainly sodium-metaborate ($NaBO_2*8H_2O$). Heating the product above 55 ^{o}C the crystalline phase released four water molecules and $NaBO_2*4H_2O$ formed. Figure 4 shows the separated wet crystals by the original and by the modified technology.

The measured specific radioactivity of the separated, dried crystalls and the unconditional clearance limit values are summarized in Table 2.

Radionuclide	Measured specific activity (Bq/g)	Unconditional clearance limit (Bq/g)
^{51}Cr	1.42E-02	30
^{54}Mn	1.19E-03	1
^{58}Co	1.01E-03	1
^{59}Fe	1.93E-03	0.9
^{60}Co	1.17E-03	0.9
^{65}Zn	2.66E-03	2
^{95}Nb	1.10E-03	0.9
^{95}Zr	1.81E-03	3
^{106}Ru	1.15E-02	1
^{110m}Ag	1.83E-03	0.9
^{124}Sb	1.83E-03	0.9
^{125}Sb	7.63E-03	1
^{134}Cs	1.66E-03	0.9
^{137}Cs	1.11E-01	2
^{144}Ce	1.02E-02	30
^{154}Eu	2.59E-02	0.9
^{3}H	2.94E-02	2000
^{14}C	1.91E-05	200
^{55}Fe	3.01E-05	100
^{59}Ni	6.20E-06	800
^{63}Ni	2.72E-04	300
^{90}Sr	3.19E-02	1
^{99}Tc	7.19E-05	1
^{129}I	1.24E-09	0.9
^{234}U	4.69E-07	0.9
^{235}U	1.71E-07	0.9
^{238}U	1.09E-07	0.9
^{238}Pu	4.83E-07	0.9
^{239,240}Pu	3.62E-07	0.9
^{241}Am	5.48E-08	0.9
^{242}Cm	4.01E-07	0.9
^{244}Cm	4.26E-07	0.9

Table 2. *The measured specific radioactivity of the separated, dried crystalls and the unconditional clearance limit values*

Based on our modification of the original wastewater treatment technology in the Hungarian Nuclear Power Plant we get beneficial results summarized as follows:

- The use of the new cesium selective ion exchanger eliminates the acidification of the evaporator bottom residue before the cesium removal by ion exchange.
- Hence we can avoid the formation of borate crystals contaminated with radionuclides of cesium etc. and the additional washing of the separated crystals for the radioactivity removal.
- According to measured specific activity data we are able to release the dried solid crystals from the NPP and could be used as non-radioactive borate chemical.

3. Chemical and radiochemical analysis of radioactive sludges fron NPP Paks

According to the international experiences the sampling process depends on the sludge characteristics. The first step of the sampling process is a previous sampling to determine the boundary between the supernatant and sludge layers. This is followed after 3-4 days by the sampling. For diluted, liquid type sludges below the supernatant layer we can detect very often a crystalline salt and amorf sludge layer too. Sampling are usually done from the top, intermediate and bottom layers using a sampling pipe and vacuum For the concentrated sludges the samples are taken from different layers of the sludge phase.

Following the sampling the sludge samples are photographed and characterized. The samples for organic content determination (TC, TOC, TIC) are collected in glass bottles, the samples for ion chromatographic analysis are stored in polyethylene botles at 4 ^{0}C. The liquid samples are analysed for pH.

We investigated two times three sludge samples taken from the tanks 02TW30B001, 02TW01B001, 01XZ06B001 of the Paks NPP. The sample characteristics are summerized in Table 3.

Sample Code	Tank code	Sample type	Sampling time
P3	02TW30B001	sludge from the evaporator, pH~13	2008. 11. 06. 11:45
P4	02TW01B001	settled sludge from diluted waste water tank, pH~8	2008. 11. 06. 11.45
P5	01XZ06B001	sludge from the wash-house waste	2008. 11. 07. 10.30
P3-2	02TW30B001	sludge from the evaporator, pH~13	2009.01.20.
P4-2	02TW01B001	settled sludge from diluted waste water tank, pH~8	2009.01.20.
P5-2	01XZ06B001	sludge from the wash-house waste	2009.01.20.

Table 3. Sludge sample characteristics

The samples P3 and P4 are seen on Picture 1. The P3 and P4 samples contained liquid phase too, while sample P5 contained only solid, consistent type phase.

Picture 1. The samples P3 and P4 shaked(left) and settled(right)

Physical chracateristics of the sludge samples

Because of the high dissolved and suspended content, high pH and other characteristics the direct determination of the sludge densities, the total solid content (TS), the dissolved and undissolved solid content (DS, UDS) was questionable. Separation of the liquid content of the composite sludge samples by vacuum filtration resulted a given amount of liquid phase remaining between the particles of the sludge sample and the determination of the total solid content of the sample is also problematic. Washing the dried sample may cause some dissolution losses. Because the above mentioned reasons we used an indirect method suggested by analysts (Ceo et al.,1990) for the determination of the densities and solid content of the samples. The results are shown in Table 4.

Sample	original sludge				centrifuged sludge			
	DS*	liquid mass	UDS**	flocculation density	DS*	liquid mass	UDS**	flocculation density
	%	g/ml	%	g/ml	%	g/g	%	g/ml
P3-2	20.417	0.971	10.174	1.139	15.022	0.847	24.415	1.179
P4-2	0.121	0.818	18.274	1.208	0.065	0.772	22.851	1.355
P5-2	-	-	-	-	-	-	-	-

(* DS-dissolved solid content, **UDS-undissolved solid content, flocculation density-undissolved solid density)

Table 4. Physical charactersitsics of the sludge samples P3-2, P4-2 and P5-2

Organic content of the samples

We determined the TOC, TC and COD values of the centrifuged at 4000g supernatant portion of the samples P3-2 and P4-2, characterizing the dissolved organic content of the sludge samples. For the TC and TOC determination we used a SHIMADZU OceaniaTOC-V CS device, and COD was determined by the potassium bicromate method using potassium-hydrogen-phtalate reference. Results are seen in Table 5.

Sample	dilution	COD	TC	TIC	TOC
		mg/l	mg/l	mg/l	mg/l
P3-2	100	3785	5271	4177	1094
P4-2	100	971.8	250.5	140.1	110.3

Table 5. Organic content of the centrifuged supernatants

It is seen that sample P3-2 contains higher organic content then sample P4-2.

Chemical composition

Samples P3-2 and P4-2 contained supernatant liquid, which was separated by centrifuging at 4000g for 15 minutes and the separated liquid phase was analysed for anions (fluoride, chloride, nitrate, phosphate and sulfate) and for cations (lithium, sodium, potassium, ammonium, calcium and magnesium) ,by ion chromatography with dilution factors between 100 and 1000. We used an IC 861 Metrohm type ionchromatograph with a conductometric detector using an *Asupp4-250* type anion, and a *C3-250 type cation exchanger columns, with a Metrohm 837* type degasser and a *Metrohm 838* type sampler.

Alkalinity (hydroxide, carbonate and hydrogen-carbonate) was determined by titrimetry. Result of the supernatant chemical analysis of samples P3-2 and P4-2 are shown in Table 6.

P3-2					
Cations			**Anions**		
	mg/1	mekv/1		mg/1	mekv/1
Na	70389.60	3354.9	F	46.27	2.67
NH$_4$	0	0	Cl	346.16	10.69
K	4021.67	112.69	NO$_3$	27094.24	478.80
Mg	0	0	PO$_4$	199.77	6.92
Ca	0	0	SO$_4$	1170.01	26.69
Mn	0	0	OH	20199.16	1301.19
			CO$_3$	44809.96	1636.66
Sum	74411.27	3467.59	Sum	93865.58	3463.64
P4-2					
Cations			**Anions**		
	mg/1	mekv/1		mg/1	mekv/1
Na	311.2	13.53	F	0	0
NH$_4$	0	0	Cl	8	0.22
K	0	0	NO$_3$	40	0.64
Mg	0	0	PO$_4$	12.2	0.38
Ca	0	0	SO$_4$	3.7	0.08
Mn	0	0	OH	0	0
			CO$_3$	263.67	8.79
			HCO$_3$	289.70	4.75
Sum	311.2	13.54	Sum	617.27	14.87

Table 6. Chemical analysis of the centrifuged supernatants of samples P3-2 and P4-2

It is seen from the ionic composition of the supernatants, that in the P3-2 sample sudium is the main cation and important anions are carbonate, hydrogencarbonate and hydroxide. P4-2 supernatant sample contains only small amount of sodium and hydrogencarbonate ions.

The chemical composition of the remaining after centrifugation solid phases and of the sample P5-2 was determined by simultaneous wasing water analysis and fusion of the solid phases using potassium-hydroxide fusion and hydrochloric acid dissolution and sodium-peroxyde-sodium-hdroxide fusion and hydrochlorid acid dissolution. Washing was completed by washing 1 g dry sample with 10 ml ultrapure water at 25 ^{0}C and 350 rpm stirring for 10 minutes, then filtered with a 0,45 micrometer size microfilter. Filtrates were analsed with ion chromatography. According to results of analysis based on five paralell measurements sodium cation and chloride, hydroxide, nitrate, phosphate and hydrogencarbonate anions are present in the washing water samples.

Chemical composition of the solid phase sludges were also determined by the fusion of the solid phases using potassium-hydroxide fusion and hydrochloric acid dissolution and sodium-peroxide-sodium-hdroxide fusion and hydrochlorid acid dissolution.

Fusion using potassium hydroxide was completed with ~1g dry sludge mixed with 5 g potassium-hydroxide and heated for 30 minutes and after cooling dissolved in 50 ml conc.

HCl and 50 ml ultrapure water. The determined potassium content was recalibrated using the potassium content of washing water samples, supposing that all potassium content is soluble in water. The total ionic content of the sludge samples P3-2 and P4-2 was calculated by summing the ionic contrations determined by wasing water and fusion solution analysis. The equivalent concentrations of the anions were calculated according to the distribution af the anions in the centrifuged supernatants of samples P3-2 and P4-2 and to the distributions of the anions in the washing water of sample P5-2.

The variances of the five repeated analysis results of this fusion was between 0,4-39% for the different ionic components.

For each sludge sample we completed also a sodium-peroxide-sodium-hydroxide fusion and a hydrochloric acid dissolution too. In the fusion process we mixed ~0.25 g dry sludge with a mixture of 1.5 g sodium-peroxide and 1 g sodium-hydroxide and heated for 15 minutes at 600 ^{0}C. After cooling the residue was dissolved with a mixture of 50 ml cc. HCl and 50 ml ultrapure water. Solutions were analyzed by ion chromatography. The variances of the five repeated analysis results of this fusion was significantly higher (23-87%) then in case of the potassium.hydroxide based fusion, so we used the results of the smaller variances.

Results are summarized in Table 7.

a) P3-2

Cations					
	KOH fusion+HCL			total (supernatant+fusion)	
	mg/g dry sludge	mg/l sludgep	mekv/l sludge	mekv/l sludge	mg/l sludge
Na	200.59	17016.05	435.17	3790.07	87132.97
NH$_4$		0	0	0	0
K	3.83	324.89	8.31	121.00	4731.58
Mg	18.82	1596.50	131.37	131.37	1596.50
Ca	62.42	5295.08	264.22	264.22	5295.09
Mn	281.28	23860.98	1963.46	1963.46	53934.36
Sum	285.66	24232.54	839.07	4306.67	98756.14
Anions					
total equivalent capacity ditributed according to supernatant distribution					
F	-	12.34	0.64	3.31	63.07
Cl	-	92.31	2.60	13.30	471.59
NO$_3$	-	7225.88	116.53	595.33	36913.83
PO$_4$	-	53.29	1.68	8.60	272.26
SO$_4$	-	312.03	6.49	33.18	1594.07
OH	-	5383.97	316.70	1617.90	27504.34
CO$_3$	-	11950.68	398.35	2035.02	61050.69
Sum	-	25030.54	843.03	4306.675	127869.90

b) P4-2

	KOH fusion+HCl			total (supernatant+fusion)	
	Cations				
	mg/g dry sludge	mg/l sludge	mekv/l sludge	mekv/l sludge	mg/lsludge
Na	39.04	4199.53	182.67	196.20	4510.73
NH_4	0	0	0	0	0
K	0	0	0	0	0
Mg	11.12	1196.18	98.43	98.43	1196.18
Ca	68.49	7367.47	367.64	367.64	7367.47
Mn	136.66	14700.52	267.58	267.58	7350.26
Sum	118.65	12763.18	648.74	662.27	13074.38
	Anions				
	total equivalent capacity ditributed according to supernatant distribution				
F	-	0	0	0	0
Cl	-	348.30	9.82	10.05	356.30
NO_3	-	1741.50	28.08	28.73	1781.50
PO_4	-	531.16	16.78	17.16	543.36
SO_4	-	161.09	3.35	3.43	164.79
OH	-	0	0	0	0
CO_3	-	11479.55	382.65	391.44	11743.22
HCO_3	-	12612.84	206.71	211.46	12902.54

c) P5-2

	KOH fusion+HCl			Total(fusion)
	Cations			
	mg/g dry sludge	mg/l sludge	mekv/l sludge	mekv/l sludge
Na	29.29	11704.87	509.13	509.13
NH_4	0	0	0	0
K	0	0	0	0
Mg	6.967	2784.153	229.10	229.10
Ca	60.99	24372.82	1216.21	1216.21
Mn	138.75	55447.28	1009.27	1009.27
Sum	97.247	38861.85	1954.44	1954.44
	Anions			
	total equivalent capacity ditributed according to washing water distribution			
F	-	0	0	0
Cl	-	1535.89	43.32	43.32
NO_3	-	1000.38	16.13	16.13
PO_4	-	21549.04	680.70	680.70
SO_4	-	3731.21	77.69	77.69
OH	-	0	0	0
CO_3	-	0	0	0
HCO_3	-	69352.12	1136.60	1136.60
Sum	-	97168.64	1954.44	1954.44

Table 7. Ionic composition of solid sludges using KOH fusion and the total sludge composition

We determined also the the undissolved oxalate content of the sludges by treating the samples first with cc. HCl for the dissolution of iron complexes, followed with a cc. nitric acid dissolution. The undissolved oxalate content of the samples P3-2, P4-2 and P5-2 was 4.177, 6.848, 23.362 meq/l accordingly.

The EDTA content of the centrifuged supernatants were determined with ion chromatography with the method suggested by analysts (Krokidis et al.,2005). The EDTA content (as Na_2H_2-EDTA*$2H_2O$) was for centrifuged supernatant samples P3-2 and P4-2 10.86 and 12.82 mmol/l accordingly. The iron and manganese content of the sludge samples were determined by AAS.

The borate content of the centrifuged supernate samples P3-2 and P4-2 was determined also with ion chromatography with the method suggested by analysts (Tapparo et. al.,1998). The borate content was for centrifuged supernatant samples P3-2 and P4-2 164.35 and 1.172 g/l accordingly.

The sludge composition was then calculated based on the ion chromatographic and titrimetric analysis of the supernatant, washing water, fusion samples and on the ICP-MS analysis. The calculated sludge compositions are summerized in Table 8.

a) P3-2

Composition	mekv/l sludge	mmol/l sludge	mg/l sludge
NaOH	1618	1618	63084.53
Na_2CO_3	2035	1017.5	107843.6
$NaNO_3$	137	137	11644.27
KNO_3	121	121	16723.8
$Ca(NO_3)_2$	264	132	13211.77
$MgCO_3$	125	62.5	2634.819
sum of ionic	4300	3088	215142.8
$Fe(OH)_3$	2279.7	759.9	81209
$Mn(OH)_2$	109.7	54.85	4879.5

b) P4-2

Composition	mekv/l sludge	mmol/l sludge	mg/l sludge
$NaNO_3$	28.73	28.73	2441.898
Na_2CO_3	163.47	81.735	8662.995
$CaCO_3$	227.93	113.965	11406.67
$Ca(HCO_3)_2$	139.71	69.855	11324.5
$Mg(HCO_3)_2$	71.79	35.895	5252.853
$MgCl_2$	10.05	5.025	478.4353
$Mg_3(PO_4)_2$	17.16	2.86	751.7733
$MgSO_4$	3.43	1.715	206.4219
Sum of ionic	662.27	339.78	40525.54
$Fe(OH)_3$	6134.34	2044.78	218523.6
$Mn(OH)_2$	581.18	290.59	25848.81

c) P5-2

Composition	mekv/l sludge	mol/l sludge	mg/l sludge
NaCl	43.32	43.32	2531.742
NaNO$_3$	16.13	16.13	1370.965
Na$_3$PO$_4$	449.68	149.8933	24573.63
Ca$_3$(PO$_4$)$_2$	231	38.5	11942.04
Ca(HCO$_3$)$_2$	985.21	492.605	79858.36
Mg(HCO$_3$)$_2$	151.4	75.7	11077.89
MgSO$_4$	77.71	38.855	4676.689
sum of ionic	1954.45	855.0033	136031.3
Fe(OH)$_3$	4572.75	1524.25	162895.3
Mn(OH)$_2$	12.742	6.371	566.73

Table 8. The calculated composition of the sludge samples

Radiochemical composition

The radiochemical composition of the sludge samples was determined using gamma- and alpha-spektrometry and liquid scintillation measurements. For the gamma-spektrometry we used an ORTEC Model GMX25P4-76-C, Gamma-X HPGe Coaxial Detector with a CarbonFiber window, connected to a multichannel anlyser ORTEC DSPEC-jr-2.0, the spectra were measured with 100 cm^3 poliethylene sample with a 3600 sec counting time. Spectra were evaluated with a Gamma Vision – 32 code. The results show, that in the P3-2 sludge ~99,5% of the gamma-activity is from ^{137}Cs, ^{134}Cs and ^{60}Co isotopes. The centrifuged supernatant contains 92-92,7% of the cesium, 14,26% of the cobalt and 91,35% of the total gamma-activity. In the P4-2 sludge ~99,4% of the gamma-activity is from ^{60}Co and ^{137}Cs, ^{134}Cs ^{54}Mn isotopes. The centrifuged supernatant contains only 0.62% of the total gamma-activity. After fusion of the solid parts of the sludges for the P3-2 sample 97% of the gamma activity is due to ^{137}Cs and ^{60}Co, while for the P4-2 sample 89% of the gamma-activity is due to ^{60}Co, 5,7% ^{137}Cs and there is also ^{54}Mn isotope present. P5-2 sample contains less activity of which 50,6% is ^{60}Co and conatins ^{54}Mn and ^{137}Cs isotopes too.

Finally we determined the alpha- and beta-emitting isotopes in the samples too using preconcentration and salt removal techniques.For the alpha-activity measurements we used TRU columns and alpha-spectrometry and for the determination of beta-activity liquid scintillation technique. Detailed description of these measurements will be submitted later. Resultst for the KOH fusion samples radionuclide analysis are shown in Table 9.

	Sample P-3-2			Sample P-4-2			Sample P-5-2	
Isotope	Act. conc. Bq/kg	σ Bq/kg	Isotope	Act. conc. Bq/kg	σ Bq/kg	Isotope	Act. conc. Bq/kg	σ Bq/kg
^{234}U			^{234}U			^{234}U		
^{238}U			^{238}U			^{238}U		
^{239,240}Pu	78.5	±8.68	^{239,240}Pu	549	±21.1	^{239,240}Pu	127	±12.7
^{238}Pu	78.1	±8.79	^{238}Pu	429	±18.5	^{238}Pu	194	±15.7
^{241}Am	73.8	±3.78	^{241}Am	771	±16.5	^{241}Am	99.8	±8.82
^{244}Cm	11.9	±1.47	^{244}Cm	124	±5.64	^{244}Cm	54.5	±5.68
^{90}Sr	21500	±1080	^{90}Sr	10200	512	^{90}Sr	20700	±1040

Table 9. The measured alpha- and beta-activities of the fused samples with KOH

4. Conclusion

The evaporator bottom residue in the NPP Paks contains high inactive salt content ($\sim$400g/dm^3) with trace amount of radioactive fission and activation products. The separation of the bulk borate and nitrate from the radioactive minor components is of great importance before solidification. The modified separation technology produces clean crystals without radioactive pollutants above the „unconditional" clearance limits. The final volume reduction factor is higher then 1000.

There are some tanks at the power plant containing sludge type radioactive waste containing more or less liquid phase too. The general physical and chemical charactersitics (density, pH, total solid, dissolved solid etc.) and chemical and radiochemical composition of these sludges are important information for volume reduction and solidification treatment of theese wastes. Based on the literature sources we have investigated and constructed a complex analysis system for the radioactive sludge and supernatant analysis, including the physical, as well as the chemical and radiochemical analysis methods. Using well known analysis techniques as ion chromatography, ICP-MS, AAS, gamma-and alfa-spectrometry and chemical alkaline fusion digestion and acidic dissolution methods we could analyze the main inorganic, organic and radioactive components of the sludges and supernatants. Determination of the mass and charge balance for the sludge samples were more difficult then for the supernantant samples. Not only are there assumptions required about the chemical form and the oxidation state of the species present in the sludge, but many of the compounds in the sludge are mixed oxides which are not directly measured. Also, the sludge is actually a slurry with a high water content. The interstitial liquid is in close contact with the sludge, and there are many ionic solubility equilibriums. The anion data for the sludge samples are based on the water soluble anions that would be available to a water wash. The water wash would not account for the insoluble hydroxides, carbonates, and mixed oxides present. The insoluble species do not contribute to the charge balance, and the cation charge is not used in the calculation. Most of the nitrate reported for the sludge is due to the interstitial liquid. Considering the limitations of these calculations, the mass balance was within the analytical error ($\pm$20%) for the sludge samples. There were three sample preparation methods used to investigate the total anion content of the sludge samples, which included water leach, potassium-hydroxide and/or sodium peroxide/sodium hydroxide fusion and acidic dissolution.

5. References

Ceo, R. N., M. B. Sears, J. T. Shor (1990). Physical characterisation of Radioactive Sludges in Selected Melton Valley and Evaporator Facility storage Tanks. *ORNL/TM – 11653*

Krokidis, A.A., et. al. (2005). EDTA Determination in Pharmaceutical Formulations and Canned Foods Based on Ion Chromatography with Supressed Conductimetric Detection. *Analytica Chimica Acta*, 535, pp. 57-63

Patzay, G.,et. al. (2006). Radioactive wastewater treatment using a mixture of TANNIX sorbent and VARION mixed bed ion exchange resin, *International Journal of Nuclear Energy Science and Technology (IJNEST)*, 2(4), 328-341,

Tapparo, A., P. Pastore, G. Bombi (1998). Ion chromatographic Determination of Borate in Aqueous Samples Together with Other Common Anions, *Analyst,* August, Vol. 123 (1771-1773)
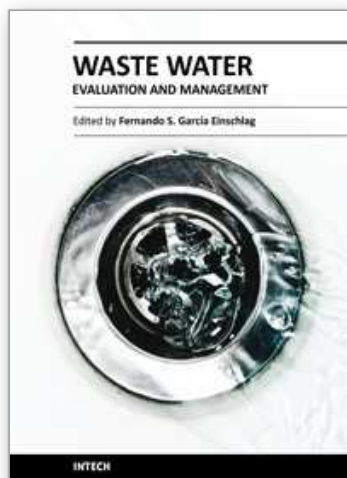
Waste Water - Evaluation and Management

Edited by Prof. Fernando Sebastián García Einschlag

Fresh water resources are under serious stress throughout the globe. Water supply and water quality degradation are global concerns. Many natural water bodies receive a varied range of waste water from point and/or non point sources. Hence, there is an increasing need for better tools to asses the effects of pollution sources and prevent the contamination of aquatic ecosystems. The book covers a wide spectrum of issues related to waste water monitoring, the evaluation of waste water effect on different natural environments and the management of water resources.

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