CESIUM RADIOISOTOPES SEPARATION IN ENVIRONMENTAL AND WASTE SAMPLES: USE OF INORGANIC/ORGANIC COMPOSITE ABSORBERS AMP-PAN, KNiFC-PAN

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Introduction

Ammonium molybdophosphate-polyacrylonitrile (AMP-PAN) and potassium-nickel hexacyanoferrate(II)-polyacrylonitrile (KNiFC-PAN) composite sorbents have been successfully used to concentrate/remove Cesium radioisotopes from large volumes of environmental or nuclear wastes samples. The advantage of embedding fine AMP and KNiFC powders in a PAN matrix is amongst others the possibility of controlling the size of particles, the porosity, the hydrophilicity, the cross-linking and the percentage of AMP/KNiFC included, making the sorbent as easy to manipulate as chromatographic resins while keeping desired properties of AMP and KNiFC such as fast Cs uptake kinetics and high Cs capacity.
This poster presents results obtained for different environmental and waste samples matrices.

Cesium Resin Properties

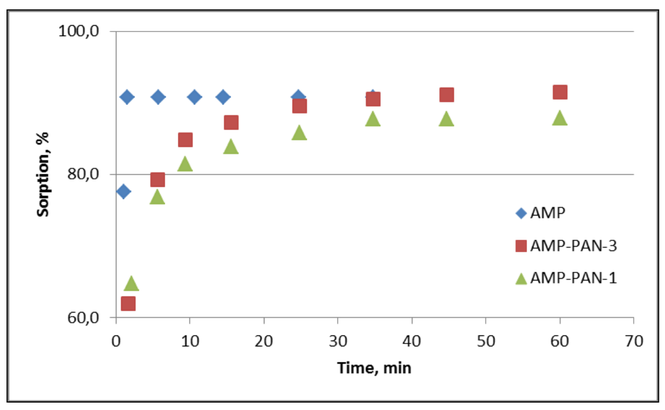


Figure 1: Cs sorption versus time of contact with AMP and AMP-PAN; 10^{-3}M CsCl in 0.1M HCl [1].
AMP-PAN-1 (58,4% in weight H_2O), AMP-PAN-3 (45,0%in weight H_2O)

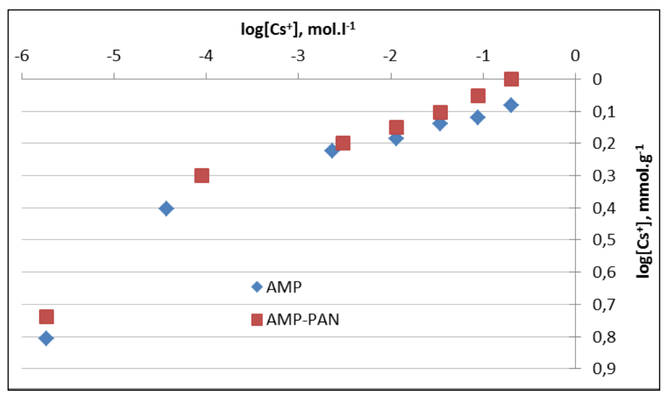


Figure 2: Cs sorption isotherm on AMP and AMP-PAN [1].

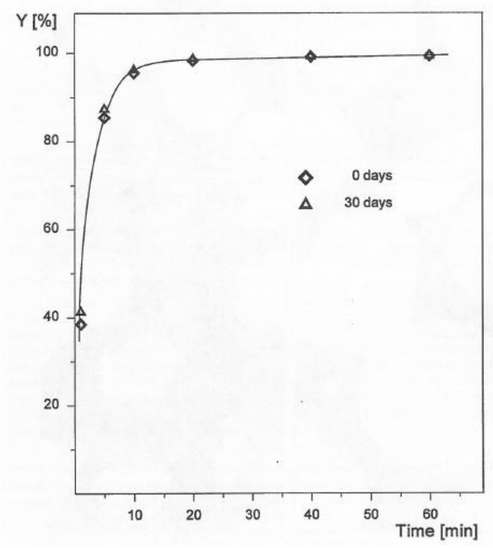


Figure 3: ^{137}Cs uptake by AMP-PAN composite absorber from 1M HNO_3 +1M $NaNO_3$ solution over time [2]

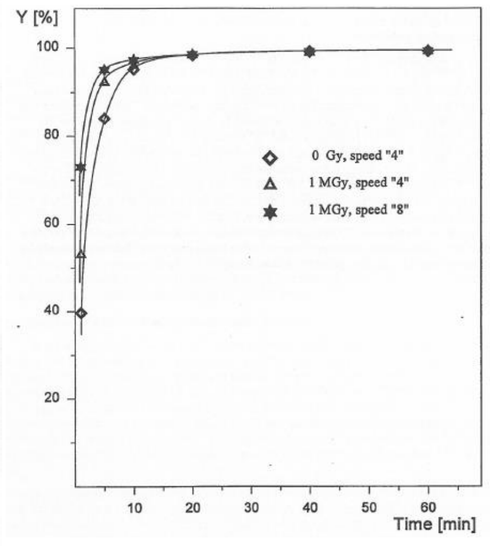


Figure 4: ^{137}Cs uptake by AMP-PAN composite absorber from 1M HNO_3 +1M $NaNO_3$ solution over time and stirring speed[2]

AMP-PAN:

- Load sample in acidic media
- Elution of Cs from AMP-PAN
  - ➢ With concentrated ammonium salt solutions (e.g. 5M NH_4Cl, 5M NH_4NO_3)
  - ➢ By dissolution and washing out of the AMP from PAN with concentrated alkaline solution (e.g. NaOH 5M)
  - ➢ Direct γ-counting of the Cs fixed on AMP-PAN

KNiFC-PAN:

- Load sample in slightly acidic to neutral media
- Direct γ-counting of the Cs fixed on KNiFC-PAN

	AMP-PAN	KNiFC-PAN
Dynamic Capacity*	64 mg Cs/g dry resin[3]	256 mg Cs/g dry resin[4]
Density	0.27 g.mL^{-1}	0.20 g.mL^{-1}
Radiation resistance	10^6 Gy	NA
Use	Acidic to neutral media (nuclear effluent waste, environmental)	Slightly acidic, neutral (environmental samples)

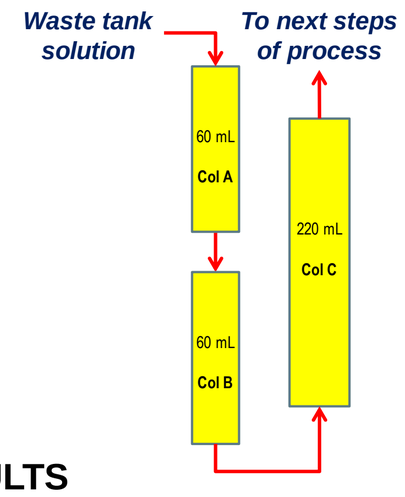
*Dynamic Capacity, $DC = \frac{([Cs^+]_0 - [Cs^+])V}{M}$
with
V=volume at a specified breakthrough of Cs (liters),
M=mass of sorbent (dry weight, grams)
$[Cs^+]_0$= initial Cs concentration (g.l^{-1})
$[Cs^+]$=Cs concentration in column effluent (g.l^{-1})

Applications

Waste tank solution[3]

CONDITIONS

- Tank waste solution at 1.5-2M acidity
- Flowrate = 22 mL/min,
- Sample volume = **45L**,
- 2x 60mL columns +1x 220mL column
- Feed pressure~20 psi,
- ~34h process
- ~130mg Cs/L
- Measure of Cs by AAS in aliquotes withdrawn
  - ➢ every hour from 0-15h process
  - ➢ every 3 hours from 15-34h process



RESULTS

- % Cs retention after the 45L have passed through the columns of AMP-PAN is **>99,83%**
- **No interference** with other species
- Ag is also retained on AMP-PAN: ~98% retention
- Fe is not retained

Seawater [4][5]

CONDITIONS

- Seawater Sample volumes= **100L**,
- Acidified pH 1-2) and raw samples,
- Column bed 25ml of AMP-PAN and KNiFC-PAN,
- Flowrate= maximum at 300ml.min^{-1},
- Gamma spectrometry measurement of the dried resin

RESULTS

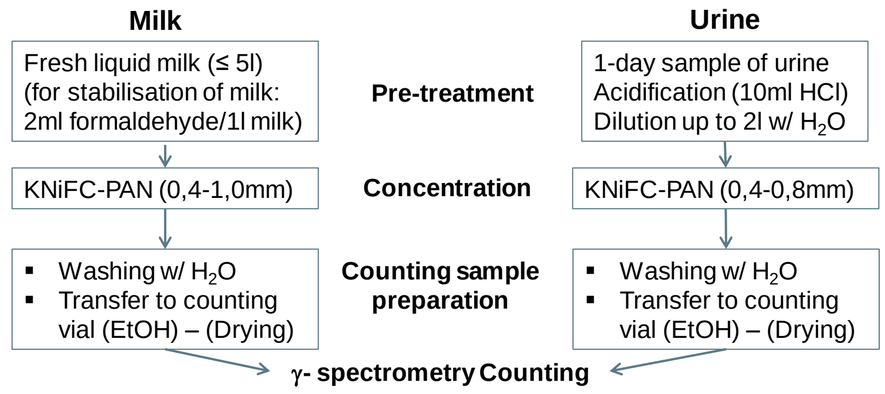
Resins	Matrix	Chemical Yield in Cs/%
AMP-PAN	Acidified seawater (pH 1)	88,1 +/- 3,3
KNiFC-PAN		92,9 +/- 1,1
KNiFC-PAN	Crude seawater	90,2 +/- 2,7

- Both resins can be used with either acidified or non-acidified seawater sample at flow-rate as high as **300ml.min^{-1}**.
- At flow-rate of 470ml.min^{-1} on KNiFC-PAN, more than **85% Cs** is recovered from a 100L raw seawater sample
- No interefrences of large amounts of Na or K on Cs retention / measurement as long as capacity of sorbent is not exceeded
- MDA for 100L samples, 50-70h counting: 0,18 Bq.m^{-3} for ^{134}Cs, and 0,15 Bq.m^{-3} for ^{137}Cs (*Coaxial HPGe, rel. Efficiency 43%, resolution 1,76keV for 1,33MeV γ-line of ^{60}Co*)

Urine/milk samples [6][7]

CONDITIONS

- Fresh milk sample volume ≤**5L** / Urine volume = 1 day sample
- Column bed 15ml of KNiFC-PAN,
- Flowrate= maximum at ≤50 ml.min^{-1},
- Gamma spectrometry measurement of the dried resin



RESULTS

- Chemical yield: **~95% Cs** on KNiFC-PAN for both milk and urine,
- **Milk**: MDA = 2mBq.l^{-1} for ^{137}Cs in 5l milk sample (HPGe detector, relative efficiency 140%, counting time 600000 s, ρ = 1g.cm^{-3}).

Conclusions

Both AMP-PAN and KNiFC-PAN have proved high efficiency to remove Cesium from different types of matrices:

- AMP-PAN resin well suited for radiocesium decontamination from large volume liquid wastes,
- AMP-PAN also fix Ag from acidic solution,
- AMP-PAN/KNiFC-PAN fix more than 90% cesium from seawater samples as large as 100L at a flowrate up to 300ml/min^{-1},
- KNiFC-PAN used for cesium separation in milk and urine with chemical yield ~95%

Literature

[1] Sebesta F., Stefula V.. Composite Ion Exchanger with Ammonium Molybdophosphate and its Properties, J. Radioanal. Nucl. Chem., Articles, Vol.140, No.1 (1990), 15-21.
[2] Sebesta F., John J., Motl A., Stamberg K. Evaluation of Polyancrylonitrile (PAN) as a Binding Polymer for Absorbers Used to Treat Liquid Radioactive Wastes, Contractor Report SAND95-2729, November 1995
[3] Herbst R.S. et al., Integrated AMP-PAN, TRUEX, and SREX Flowsheet Test to Remove Cesium, Surrogate Actinide Elements, and Strontium from INEEL Tank Waste Using Sorbent Columns and Centrifugal Contactors, INEEL/EXT-2000-00001, Janurary 2000
[4] Pike et al., Extraction of Cesium from Seawater off Japan using AMP-PAN Resin and Quantification via Gamma Spectrometry and Inductively Coulped Mass Spectrometry, J. Radioanal. Nucl. Chem, DOI 10.1007/s10967-012-2014-5, 2012
[5] Kamenik J. et al., Fast Concentration of Dissolved forms of Cesium Radioisotopes from Large Seawater Samples, J. Radioanal. Nucl. Chem, DOI 10.1007/s10967-012-207-4, 2012
[6] Sebesta et al., Separation and Concentration of Contaminants using Inorganic-Organic Composite Absorbers, 2nd International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe, September 20-23, 1994 – Budapest,Hungary.
[7] Kamenik J. et al., Long Term Monitoring of 137Cs in Foodstuffs in the Czech Republic, Applied Rad. Isotopes., 67 (2009) 974-977

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