I Always Wanted A Cs Resin

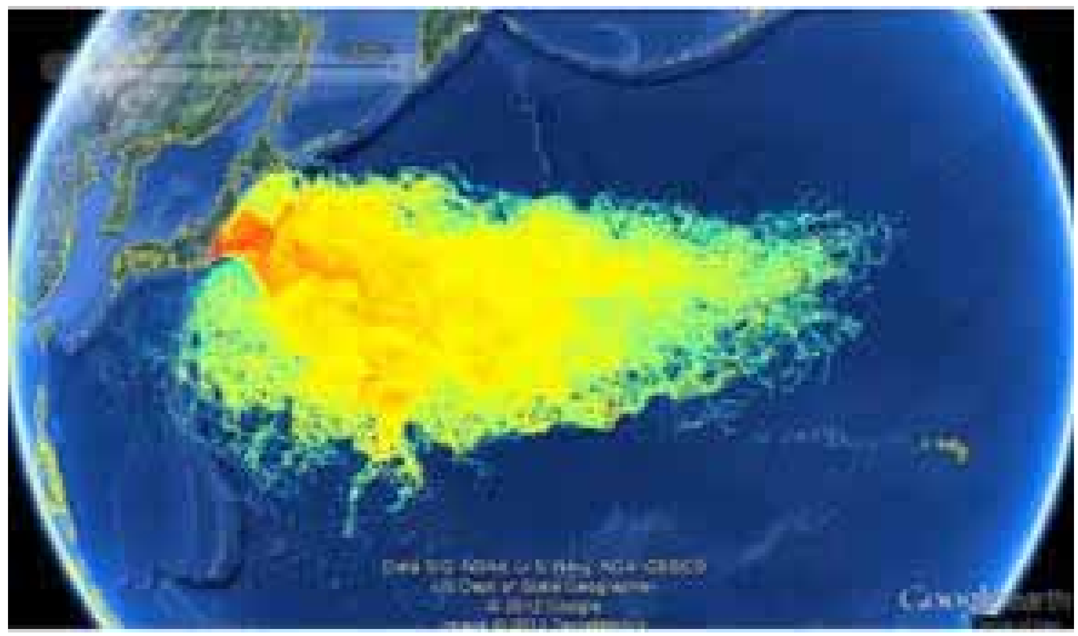
S. Happel, A. Bombard
Presented and Edited for the RRMC by Larry Jassin- Eichrom

Important Stuff

- Phil's Commandments and Observations
  1. Thou shall always strive to separate the minor constituent from the major constituents
  2. All liquid extractants eventually turn yellow
  3. When all else fails, change the diluent
  4. No amount of careful planning will ever replace dumb luck
- Bill Burnett is worried…
  – Going to teach in China, will his jokes work???
  – FSU vs. Miami, November 2, Go Canes!
- Mike Fern paid hush money, but…
  – Wisconsin 35 Northwestern 6

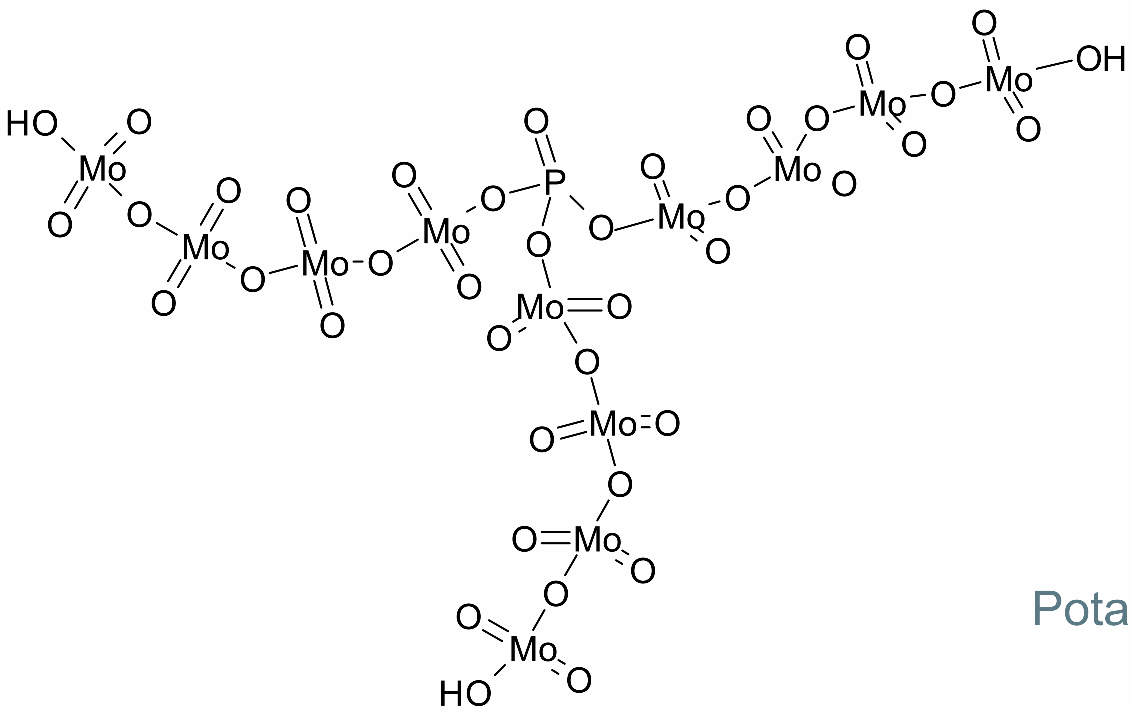
So Why Would Eichrom want a Cs Resin?

- Radwaste Treatment from Nuclear operations
- Sample preparation of high level radioactive samples
- Effluent monitoring
- Preconcentration of seawater

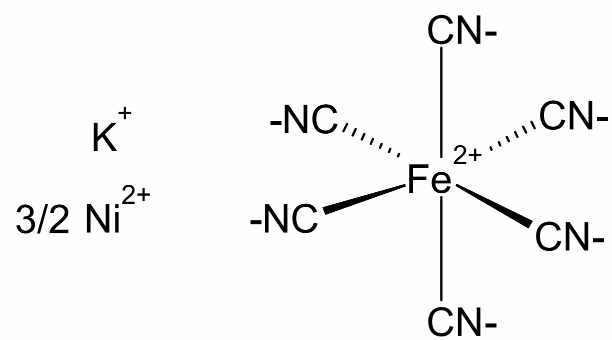


Introduction

- ✓ AMP-PAN and KNiFC-PAN developped by Dr Sebesta from CVUT (Czech Republic)
- ✓ AMP and KNiFC known to strongly bind Cs
- ✓ Embedded in organic matrix (Polyacrylnitrile, PAN)



Ammonium **M**olybdo**P**hosphate



Potassium(**K**) **Ni**ckel **F**erro**C**yanate

Comparison AMP/AMP-PAN

- Sebesta and Stefula check differences between fine AMP and AMP-PAN resin (Cs kinetics and capacity) => **SIMILAR RESULTS OBTAINED**

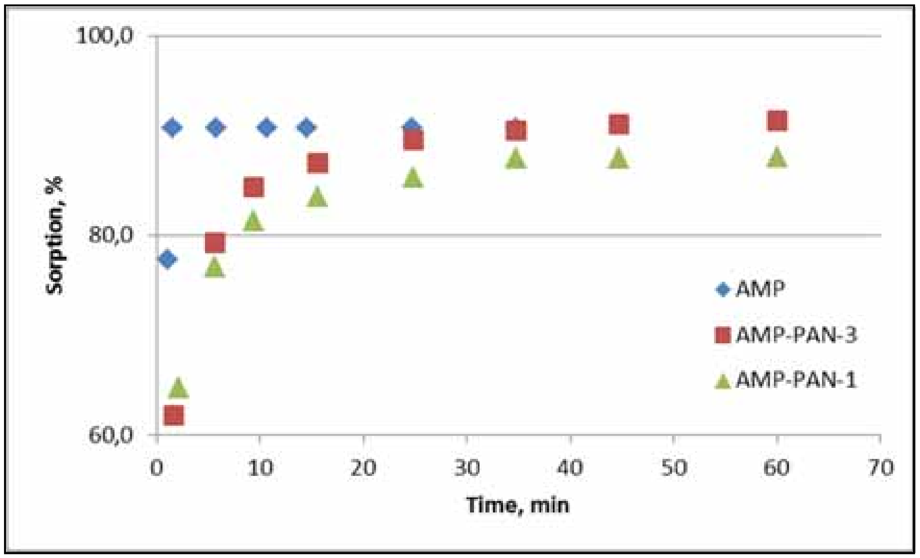


Figure 1: Cs sorption versus time of contact with AMP and AMP-PAN; 10^{-3}M CsCl in 0.1M HCl [1].
AMP-PAN-1 (58.4% in weight H_2O), AMP-PAN-3 (45.0%in weight H_2O)

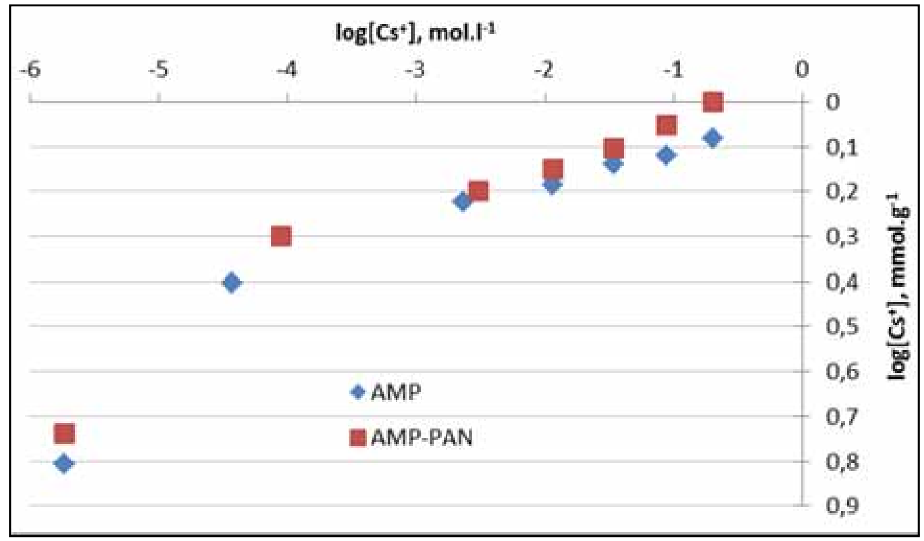


Figure 2: Cs sorption isotherm on AMP and AMP-PAN [1].

[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.

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PAN Support Properties[2]

- PAN chosen for fast, simple and cheap synthesis
- Typical properties of PAN polymers:
  - Hardness, stiffness
  - Resitant to most solvents and chemicals, U.V., heat, microorganisms
  - Radiation stability (under radiation, increase cross-linking of the polymer)
  - Soluble in aprotic solvents
  - Hydrolysis of PAN is enhanced when
    - in solution,
    - at temperatures above 90°C for acidic, neutral media and between 30-50°C in alkaline media,
    - In the presence of carboxyl and carboxamide groups

[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

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Cs Resins Properties 1/3

	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)

The inclusion in PAN matrix allows

- -Stabilisation of the fine powders in a polymeric organic support
- -Control of particle size (granulometry), porosity and cross-linking
- -% AMP/KNiFC in the final sorbent

*Dynamic Capacity, *DC* = $\frac{([Cs^+]_0 - [Cs^+])V}{M}$ with

V=volume at a specified breakthrough of Cs (liters),
$[Cs^+]_0$= initial Cs concentration ($g.l^{-1}$)

M=mass of sorbent (dry weight, grams)
$[Cs^+]$=Cs concentration in column effluent ($g.l^{-1}$)

[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] Kamenik J., Comparison of Some Commercial and Laboratory Prepared Caesium Ion-Exchangers, Czechoslovak Journal of Physics, Vol.53 (2003), Suppl.A, A571-A576

Cs Resins Properties 2/3

- AMP-PAN:
  - Fast kinetics, radiation resistant, stable in acidic media

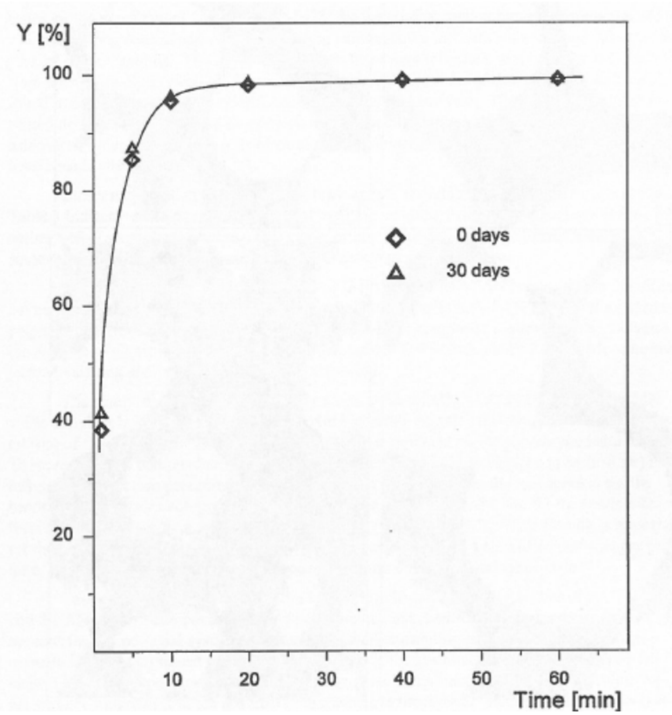

Figure 1: Dependence uptake of ^{137}Cs by AMP-PAN composite absorber from 1M HNO_3 +1M $NaNO_3$ solution over time [2]

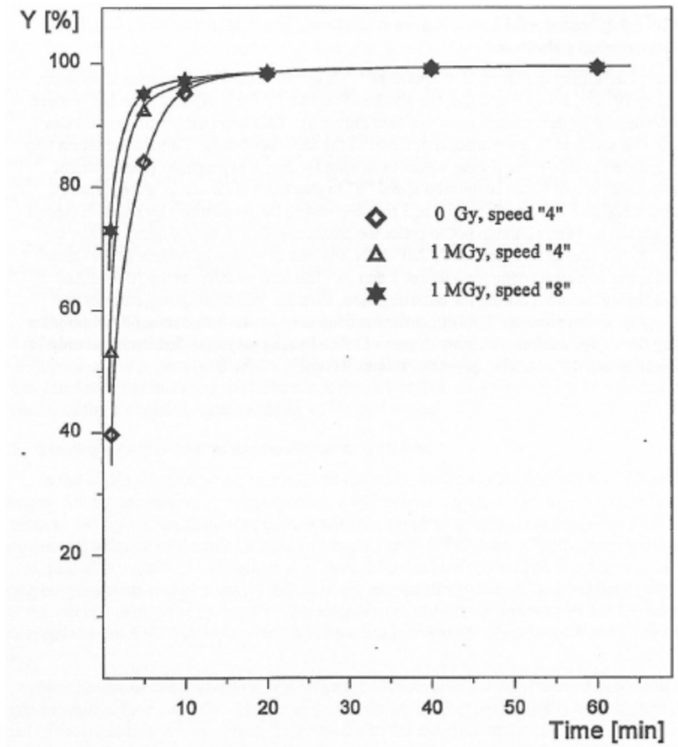

Figure 2: Dependence uptake of ^{137}Cs by AMP-PAN composite absorber from 1M HNO_3 +1M $NaNO_3$ solution over time and speed of stirring [2]

[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

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Cs Resins Properties 3/3

- 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 matrix with concentrated alkaline solution (e.g. 5M NaOH)
  - Direct γ-counting of the Cs fixed on AMP-PAN
  - Elements retained on AMP-PAN resin (in 40L of effluent sample) : Cs(99.87%), Ag(98.9%), Zr(10.5%) – other elements not retained.
- KNiFC-PAN:
  - Load sample in slightly acidic to neutral media
  - Direct γ-counting of the Cs fixed on KNiFC-PAN

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Cs Resins Applications

- Liquid radioactive waste samples
- Seawater samples
- Milk/urine samples

AMP-PAN for Cs separation in liquid radioactive wastes[2][3][5][6][7]

- Resistance to radiation makes AMP-PAN well suited for measurement of Cs in liquid radioactive wastes
- AMP-PAN = first step in general process to separate RN in nuclear tank wastes

[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

[5] Brewer K.N. et al., AMP-PAN column Tests for the Removal of 137Cs from Actual and Simulated INEEL High-Activity Wastes, Czechoslovak Journal of Physics, Vol. 49 (1999), Suppl. S1, 959-964

[6] John J. et al., Application of a New Inorganic-Organic Composite Absorbers with Polyacrylonitrile Binding Matrix for the separation od Radionuclides from Liquide Radioactive Wastes, Chemical Separation Technologies and Related Methods of Nuclear Waste Management, Kluwer Academic Publishers, Netherlands 1999, 155-158

[7] Todd T.A. et al. Cesium sorption from Concentrated acidic Tank Wastes using Ammonium molybdophosphate-polyacrylonitrile composite sorbents, J. Radioanal. Nuc. Chem., Vol.254, No.1 (2002) 47-52

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AMP-PAN for Cs separation in liquid radioactive wastes[3]

- Procedure: Tank wastes
  - Simulated (130mg $Cs.L^{-1}$) tank wastes
  - About 45L of simulated tank waste solution processed over about 34 hours
  - Flow rates:
    - Feed sample: $1.32 L.h^{-1}$,
  - 2 columns of 60 mL and 1 column of 220 mL (*polishing column to fix Cs traces breakthrough from the 60mL columns*) in series

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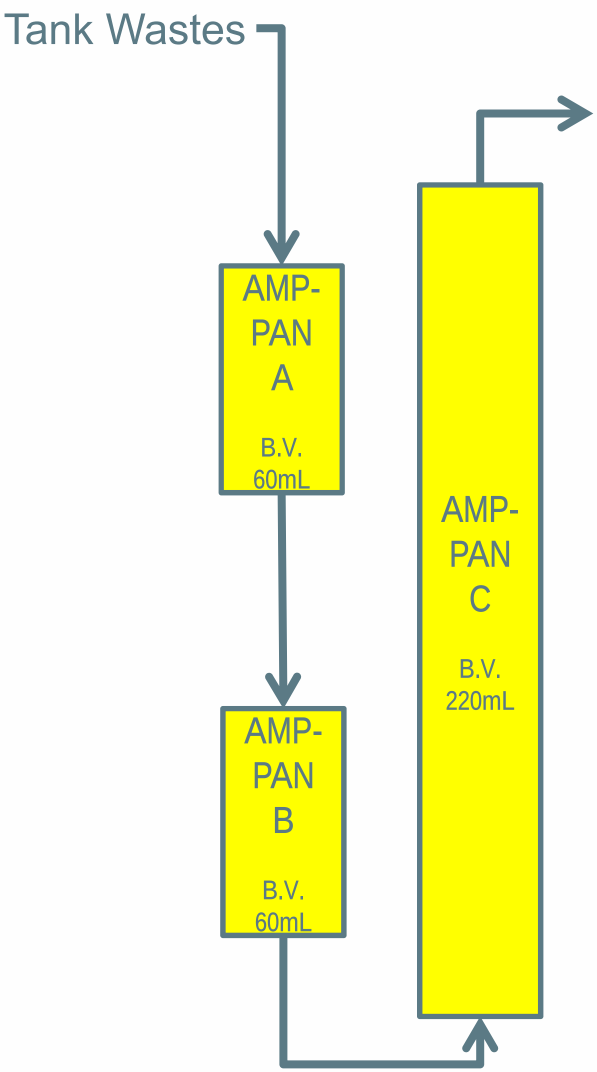
AMP-PAN for Cs separation in liquid radioactive wastes[3]



Eluant to next steps of the process:
-TRUEX (actinides removal)
-SREX (Sr removal)

Results simulated sample:

- Cs removal > 99,83%

Retained on AMP-PAN but to be further checked:

-98,91% Ag retained as Ag+ or as precipitate in AgNO3?? No conclusion

-11% Zr, but very near limit of detection

Other elements tested not retained (Fe, Sr, F, Ni, Ba, Cr,...)

AMP-PAN for Cs separation in liquid radioactive wastes[2][3][5][6][7]

- Procedure: Tank wastes
  - Simulated (100Bq.mL^{-1} ^{137}Cs) and real tank wastes
  - Flow rates:
    - Feed sample: 39-41mL.h^{-1},
    - Wash solution (0,1M KNO_3/0,1M HNO_3): 39-41 mL.h^{-1},
    - Elution solution (5M NH_4NO_3/0,1M HNO_3): 4-6 mL.h^{-1}.
  - 2 cycles on one 1,5ml column:
    - 1 cycle consists in:
      - feeding waste solution (up to 1600ml) on column
      - Washing of the column
      - Cs elution

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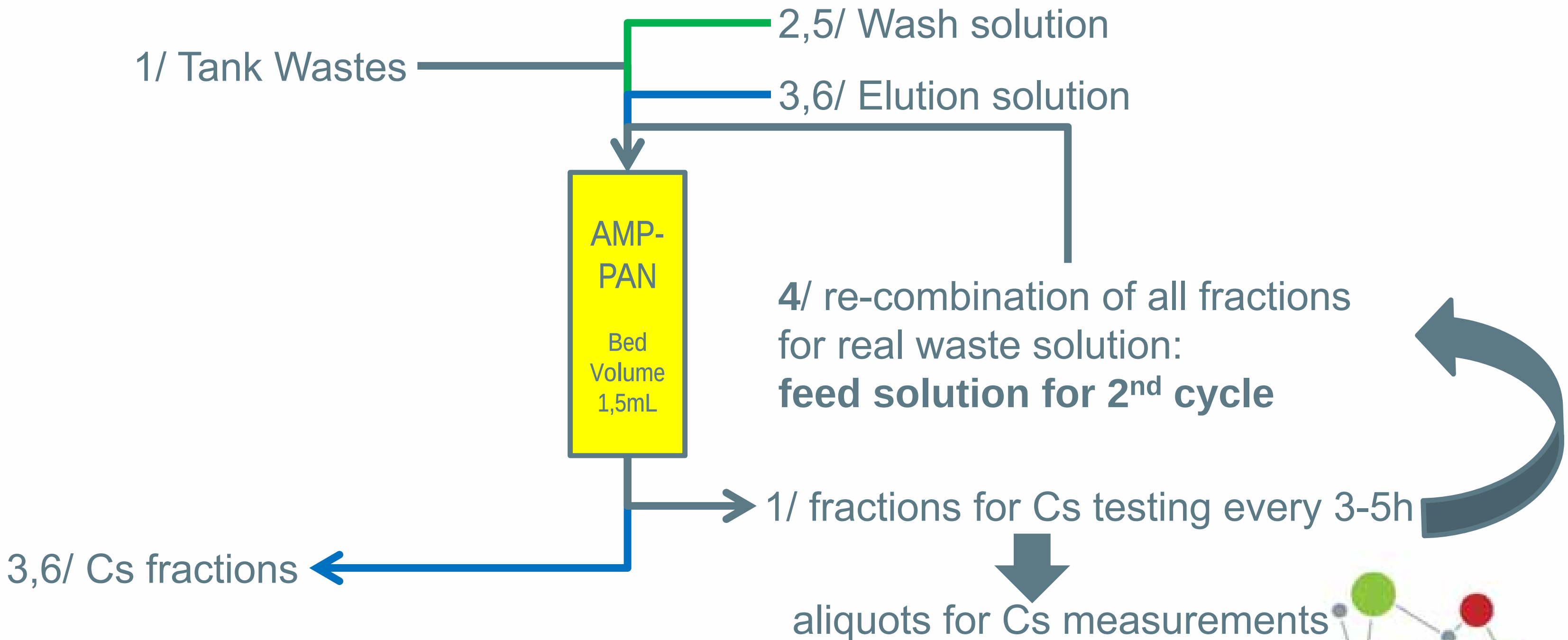
AMP-PAN for Cs separation in liquid radioactive wastes[2][3][5][6][7]

- Procedure: Tank wastes
  - Real waste solution volume: up to 1,6l
  - Simulated waste solution volume: up to 6,1l



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AMP-PAN for Cs separation in liquid radioactive wastes[2][3][5][6][7]

- Results real sample
  - Cs breakthrough=0.15% after 1500ml load after 1st cycle
  - Cs breakthrough=0.53% after 1245ml load after 2nd cycle
    - Decontamination factor >3000
  - Average Cs recovery in elution fraction (2 cycles): 87%
  - 83% Cs eluted in 45ml 5M NH_4NO_3 (in 1st cycle)

T-AB2

- Results simulated sample
  - Cs breakthrough=50% after 4800ml load after 1st cycle
  - Cs breakthrough=50% after 4050ml load after 2nd cycle
  - More than 70% Cs eluted in 75ml 5M NH_4NO_3/0,1M HNO_3 (in 1st cycle),
  - ~40% Cs remained fixed on AMP-PAN (non-elutable Cs) => elution conditions of Cs to be optimised

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Slide 16

T-AB2 it seems that on the simulated sample, more Cs remained fixed on the resin than with real sample for which this % is still about 25-27% (the 25% being obtained after collecteing 2% Cs from AMP-PAN dissolution).
No yield of Cs indicated for the simulated sample. and besides for this simulated sample, the 2nd feed initiating the 2nd cycle is made with a "fresh" simulated solution whereas for th ereal sample it was just the gathering of theunused parts of the fractioning meaning most of the 2nd feed is not high in Cs compared to fresh feed.
TRISKEM - Aude BOMBARD, 10/3/2013

Cs measurements in Seawater [8][9]

- Procedure:
  - Seawater Sample volumes: 100L,
  - Acidified (pH 1-2) and raw samples,
  - Column bed 25ml of AMP-PAN and KNiFC-PAN,
  - Flowrates up to 300ml.min^{-1},
  - Gamma spectrometry measurement

[8] 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

[9] 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

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Cs measurements in Seawater [8][9]

- 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	Non-acidified seawater	90.2 +/- 2.7

- Both resins can be used with either acidified seawater samples at flow-rates as high as 300ml.min^{-1}.
  - KNiFC-PAN can also be used for non-acidified sea water
- Greater 85% Cs recovered on KNiFC-PAN from a 100l raw seawater sample at flow-rate of 470ml.min^{-1} No interferences of large amounts of Na or K on Cs 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,
  - 0.15 Bq.m^{-3} for ^{137}Cs.

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Cs Measurements in Milk, Urine [10][11]

Milk

- Fresh liquid milk (≤ 5l) (for stabilisation of milk: 2ml formaldehyde/1l milk)

↓

- KNiFC-PAN (0.4-1.0mm)
- Bed resin = 15 ml
- Flowrate ≤ 50ml.min^{-1}

↓

- Washing w/ H_2O
- Transfer to counting vial (EtOH) – (Drying)

Urine

- 1-day sample of urine
- Acidification (10ml HCl)
- Dilution up to 2l w/ H_2O

↓

- KNiFC-PAN (0.4-0.8mm)
- Bed resin = 15 ml
- Flowrate ≤ 50ml.min^{-1}

↓

- Washing w/ H_2O
- Transfer to counting vial (EtOH) – (Drying)

Pre-treatment

Concentration

Counting sample preparation

γ- spectrometry Counting

[10] 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.

[11] 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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Cs Measurements in Milk, Urine [8][9]

- 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}).

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Summary

- AMP-PAN resin well suited for radiocesium decontamination from large volume liquid wastes: decontamination factor >3000.
- AMP-PAN/KNiFC-PAN retained more than 90% cesium from seawater samples as large as 100L at a flowrates up to 300ml/min^{-1},
- KNiFC-PAN used for cesium separation in milk and urine with chemical yield ~95%

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"Our greatest weakness lies in giving up. The most certain way to succeed is to try just one more time."
— Thomas A. Edison

Conference Golf Outing
Thursday, depart 2:10 from Lobby


Questions?