Cesium Resins:

- AMP-PAN
- KNiFC-PAN

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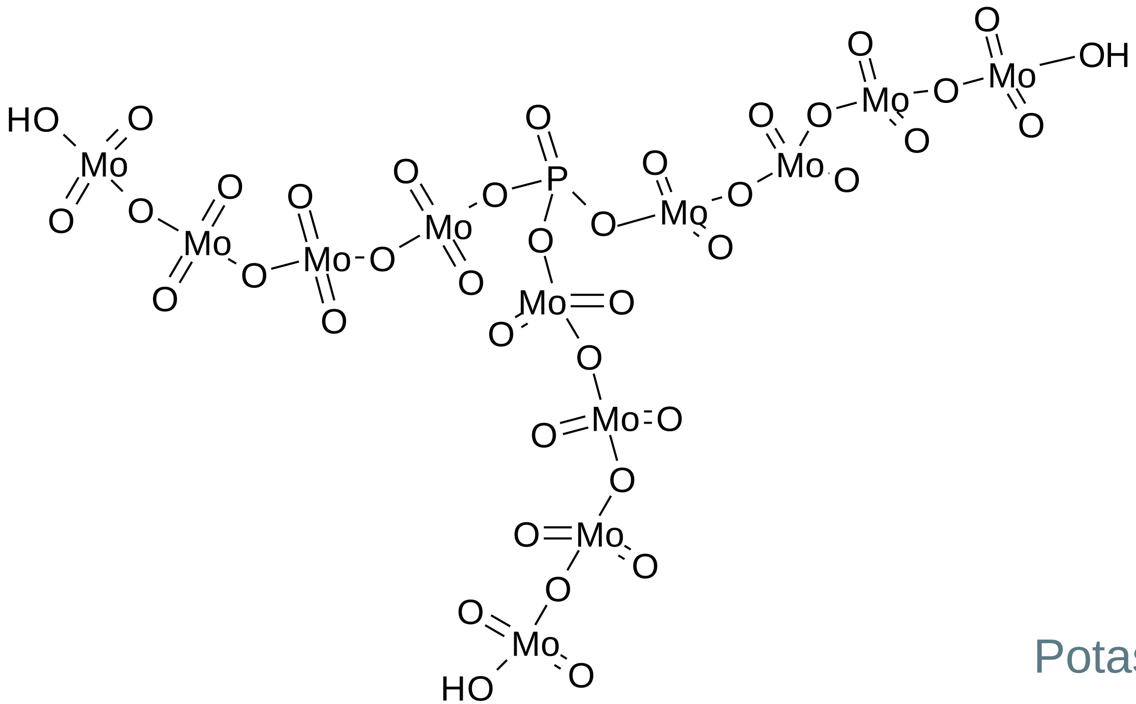
Outline

- Scope
- Comparison AMP/AMP-PAN
- PAN Support Properties
- Cs Resins Properties
- Summary

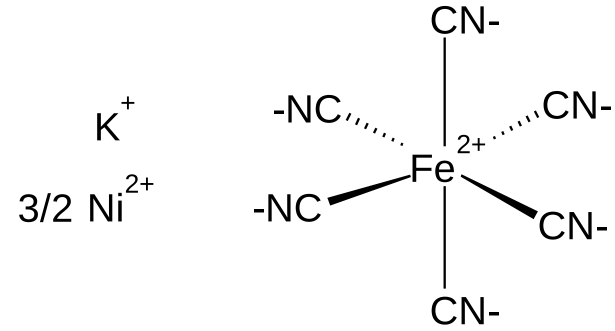
Scope

AMP-PAN and KNiFC-PAN developped by Dr Sebesta from CVUT (Czech Republic)

AMP and KNiFC known for their property to strongly bind Cs



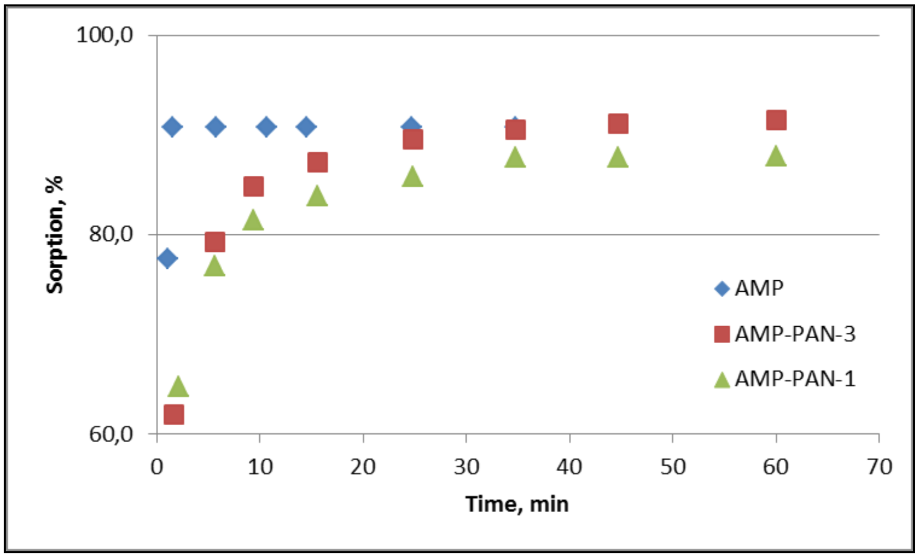
Ammonium **M**olybdo**P**hosphate



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**



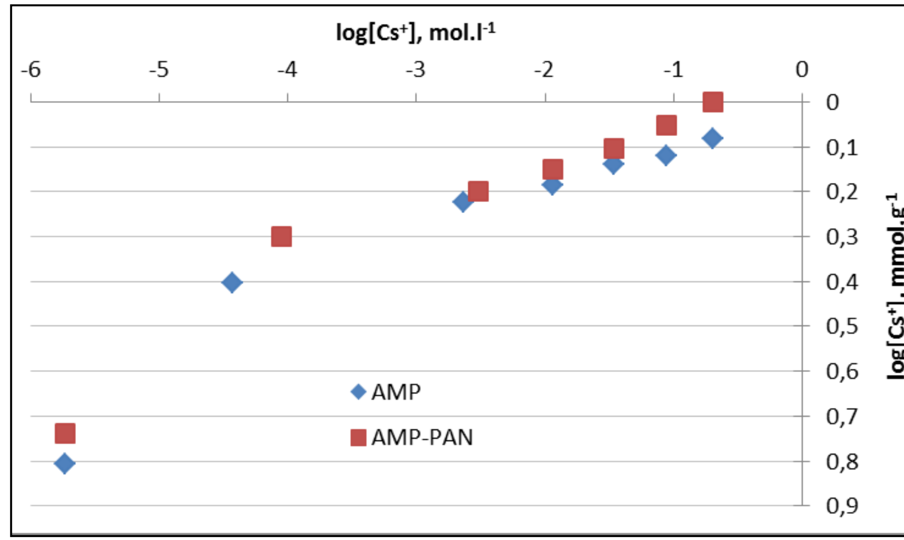


Figure 1: Cs sorption versus time of contact with AMP and AMP-PAN; 10^{-3}M CsCl in 0.1M HCl [1].
AMP-PAN-1 (58,4% in weight H_2O), AMP-PAN-3 (45,0%in weight H_2O)

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.

PAN Support Properties[2] 1/2

- Polyacrylonitrile (PAN => CH_2=CHCN) chosen for its fast, simple and cheap synthesis
- Typical properties of PAN polymers:
  - Hardness, stiffness
  - Resitant to most solvents and chemicals,to U.V., heat, microorganisms
  - Slow to burn
- PAN polymers form H-Bonds, transition metal ion complexes, donor-acceptor complexes

[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

PAN Support Properties[2] 2/2

- Radiation stability (under radiation, increase cross-linking of the polymer)
- Chemical stability:
  - Soluble in aprotic solvents
  - Hydrolysis of PAN is enhanced when PAN is
    - 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

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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

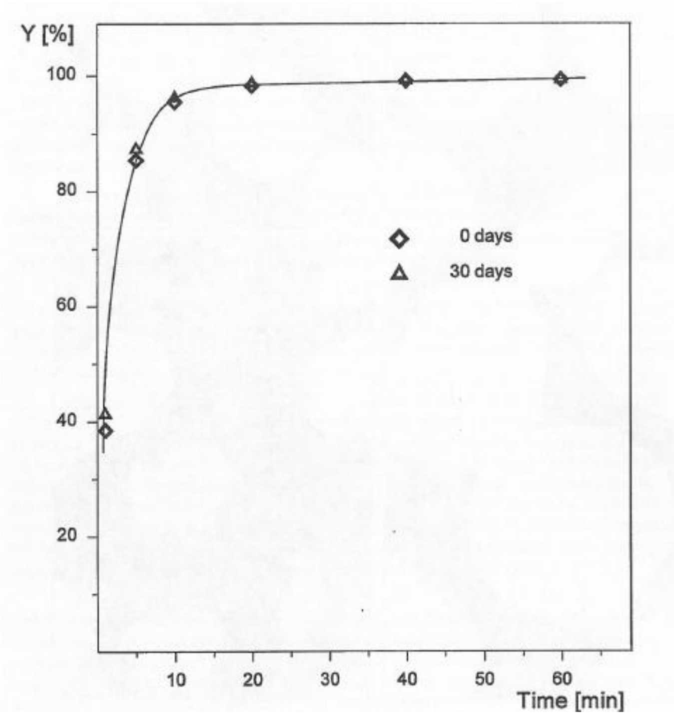

Figure 1: Dependence uptake of ^{137}Cs by AMP-PAN composite absorber from 1M HNO_3 +1M $NaNO_3$ solution over time [2]

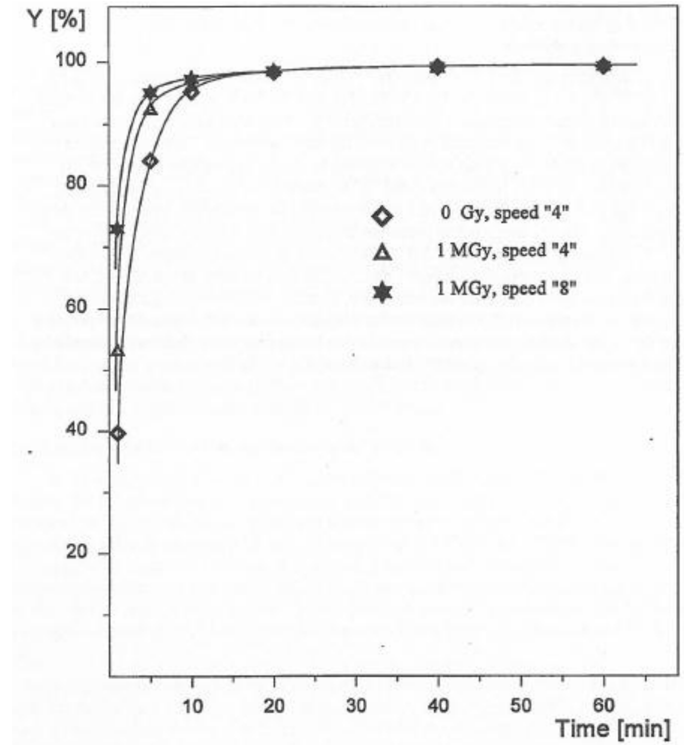

Figure 2: Dependence uptake of ^{137}Cs by AMP-PAN composite absorber from 1M HNO_3 +1M $NaNO_3$ solution over time and speed of stirring [2]

[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 from PAN of the AMP 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

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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][5][6][7]

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

[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

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

- Procedure: Tank wastes
  - Simulated ($100 Bq.ml^{-1}$ ^{137}Cs) and real
  - Flowrates:
    - Feed sample: $39\text{-}41 mL.h^{-1}$,
    - Wash solution ($0,1M$ KNO_3/$0,1M$ HNO_3): $39\text{-}41$ $mL.h^{-1}$,
    - Elution solution ($5M$ NH_4NO_3/$0,1M$ HNO_3): $4\text{-}6$ $mL.h^{-1}$.
  - 2 cycles for each 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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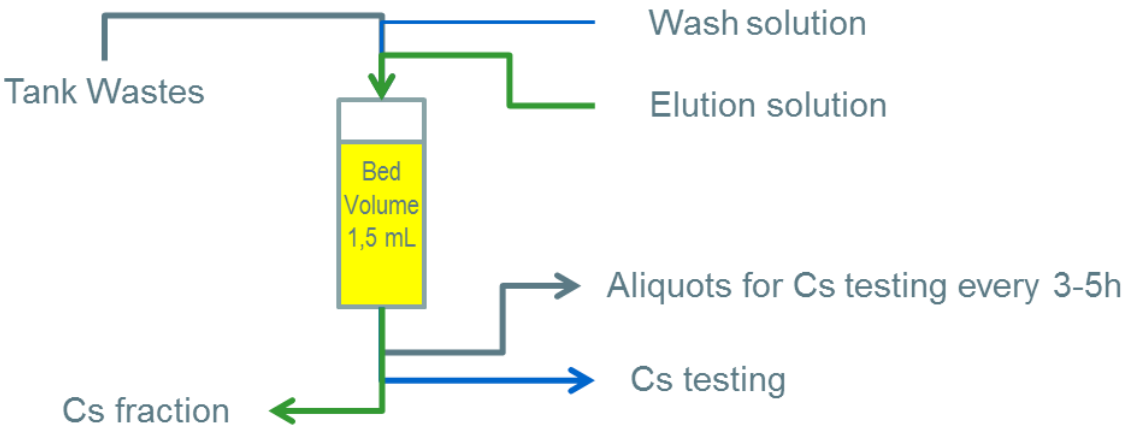
AMP-PAN for Cs separation in liquid radioactive wastes[2][5][6][7]

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



AMP-PAN for Cs separation in liquid radioactive wastes[2][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
- Results simulated sample
  - Cs breakthrough=50% after 4800ml load after 1st cycle
  - Cs breakthrough=50% after 4050ml load after 2nd cycle
  - Average Cs recovery in elution fraction, 1st cycle: >70%
  - More than 70% Cs eluted in 75ml 5M NH_4NO_3/0,1M HNO_3,
  - ~40% Cs remained fixed on Cs => elution conditions of Cs to be optimised

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Cs measurements in Seawater [8][9]

- Procedure:
  - Seawater Sample volumes: 100L,
  - Acidified (pH 1-2) and crude samples,
  - Column bed 25ml of AMP-PAN and KNiFC-PAN,
  - Flowrate: maximum at 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	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 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.

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

Milk		Urine
▪Fresh liquid milk (≤ 5l) (for stabilisation of milk: 2ml formaldehyde/1l milk)	**Pre-treatment**	▪ 1-day sample of urine ▪ Acidification (10ml HCl) ▪ Dilution up to 2l w/ H_2O
▪ KNiFC-PAN (0,4-1,0mm) ▪ Bed resin = 15 ml ▪ Flowrate ≤ 50ml.min^{-1}	**Concentration**	▪ KNiFC-PAN (0,4-0,8mm) ▪ Bed resin = 15 ml ▪ Flowrate ≤ 50ml.min^{-1}
▪ Washing w/ H_2O ▪ Transfer to counting vial (EtOH) – (Drying)	**Counting sample preparation**	▪ Washing w/ H_2O ▪ Transfer to counting vial (EtOH) – (Drying)

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

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}).

Summary

- AMP-PAN resin well suited for radiocesium decontamination from large volume liquid wastes: decontamination factor >3000.
- 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%

Thank you for your attention,

Any questions?