55Fe, 63Ni and 59Ni in old nuclear reactor pressure vessel steel samples

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Contents

Introduction

- Study part of KYT 2018 VAMMA program.
- Collaboration with HYRL, VTT, Fortum and TVO.
- Goal of VAMMA: Determine the radionuclide inventory of decommissioning waste, determine the best methods for analysis and detection of the radionuclides, and create scaling factors for difficult to measure radionuclides.
- Goal of this study: Determine a suitable method for the separation and analysis of radionuclides Fe-55, Ni-63 and Ni-59 and test it on real decommissioning steel.
- Study is part of a project to develop analysis methods for the decommissioning of FiR 1 research reactor in Otaniemi.

Fe-55

- Formed in neutron activation reactions 54Fe(n,γ)55Fe and 56Fe(n,2n)55Fe.
- $T_{1/2}$ = 2.7 y.
- Decay mode: Electron capture.
- Emits 5.9 keV x-rays and 5.2 keV Auger electrons.
- Low energy requires separation from other radionuclides. Possible to measure with LSC.

Ni-63

- Formed in neutron activation reactions 62Ni(n,γ)63Ni and 63Cu(n,p)63Ni.
- $T_{1/2}$ = 100 y.
- Pure beta decay. Emits 66.9 keV electron upon decay.
- Easy to measure with LSC.

Ni-59

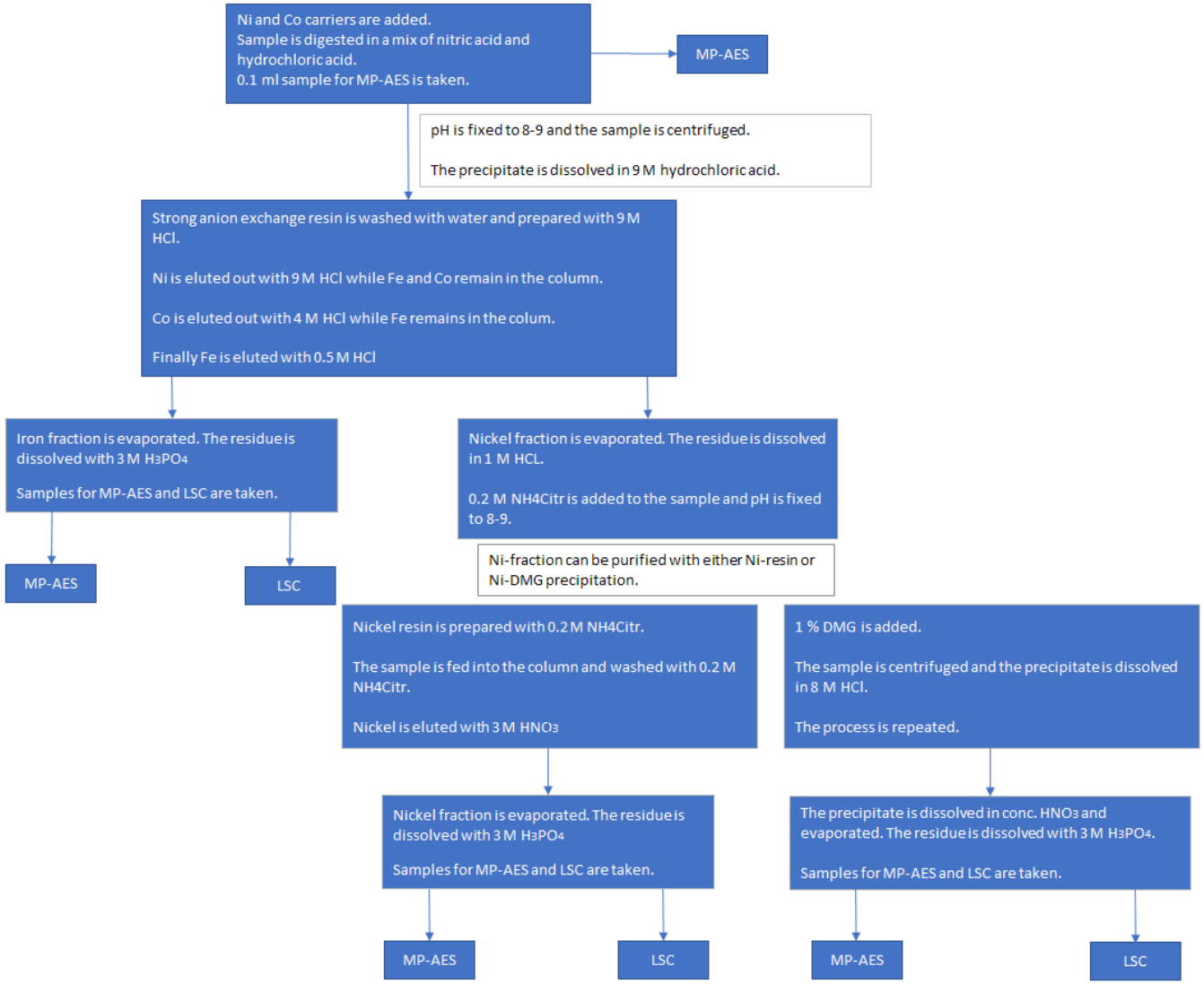
- Formed in reaction 58Ni(n,γ)59Ni.
- $T_{1/2}$ = 76 000 y.
- Decays by electron capture. Emits 6.9 keV x-rays and 6.1 keV Auger electrons.
- Cannot be measured with LSC due to Ni-63 present (Ni-63/Ni-59 activity ratio over 100).
- Needs to be measured with x-ray spectrometry or with mass spectrometric techniques.

Samples

- 16 0.2 g steel samples provided by VTT.
- Half of the samples were radioactive and half inactive. The samples were from reactor pressure vessel.
- Two different types of steel that were archived samples from BWR and VVER reactors.

Analysis

- Original plan:
  - Metals separated from group I and II elements via hydroxide precipitation.
  - Metals separated from each other in anion exchange column by controlling the concentration of acid washing solution.
  - Nickel fraction purified with one of two methods: Nickel resin or Ni-DMG precipitation.
- MP-AES was used to determine chemical yield and LSC to measure the activity of Fe-55 and Ni-63.
- X-ray samples can be prepared by pecipitating nickel onto a filter, electroplating on a metal disc or evaporating on a small container.
- Inactive samples were used to fine tune the separation process



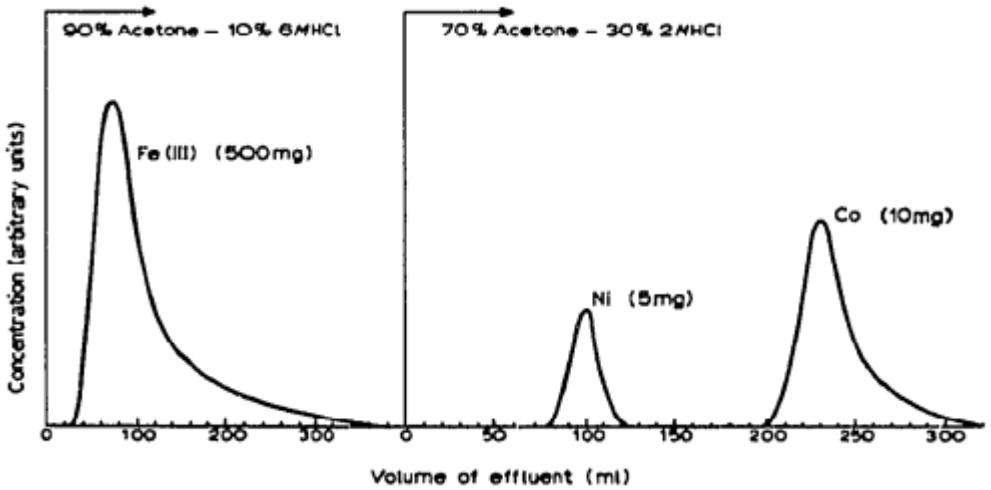
- In the first analyses with inactive steel it was found that initial 40 ml of ion exchange resin was not enough to retain all iron, requiring two anion exchanges for nickel fraction. In the analyses of active steels the amount of resin was increased to 60 ml.

- Wash and elution solution volumes were also increased to match the increasing volume of resin.

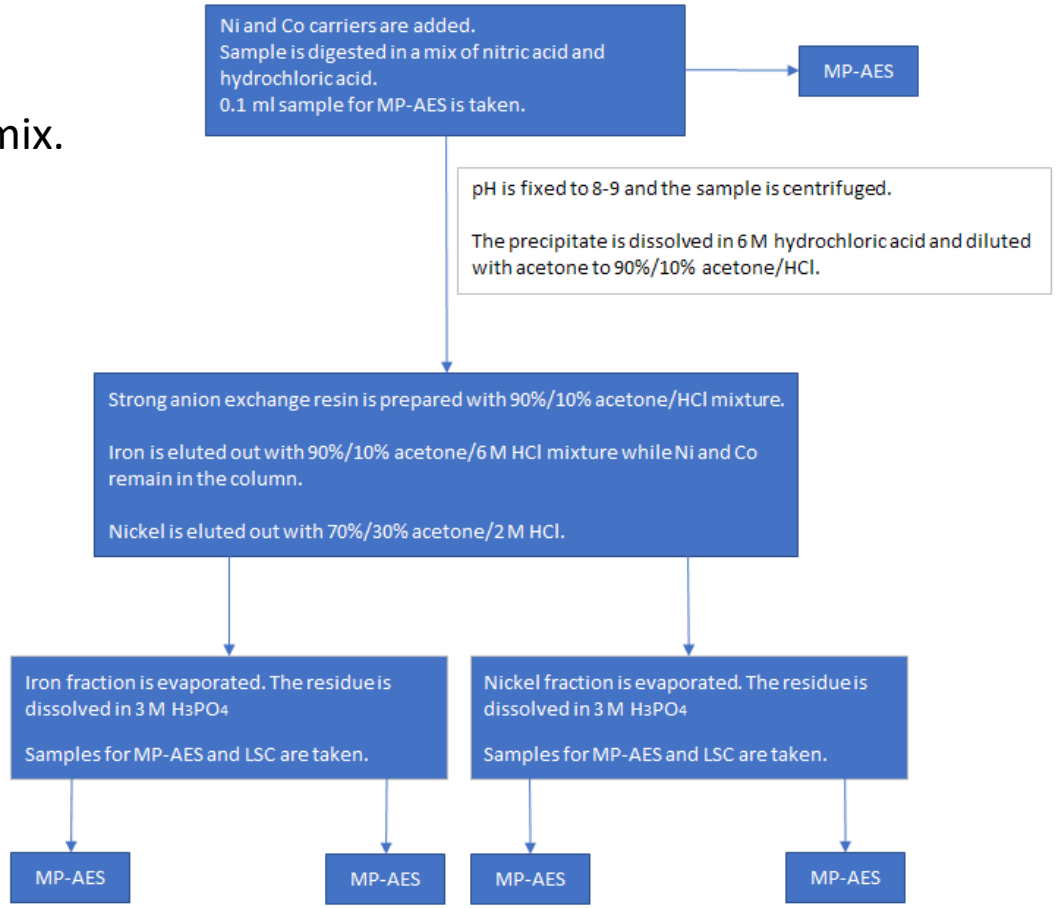
- In the analysis of active samples, Ni-resin didn’t retain all of the nickel and some of it ended up in wash solution.

- Enough Co-60 ended up in both iron and nickel fractions to ruin the measurements → Need to find a way to purify the metal fractions.

- When in 90% acetone – 10% 6M HCl medium, nickel and cobalt absorb strongly in anion exchange resin, while iron is not absorbed.
- This same solution can be used to separate iron from other metals.
- Both nickel and cobalt are eluted with 70% acetone – 30% 2M HCl mix. Nickel is eluted before cobalt, giving a window where nickel can be separated from cobalt.
- Suitable for large amounts of iron.

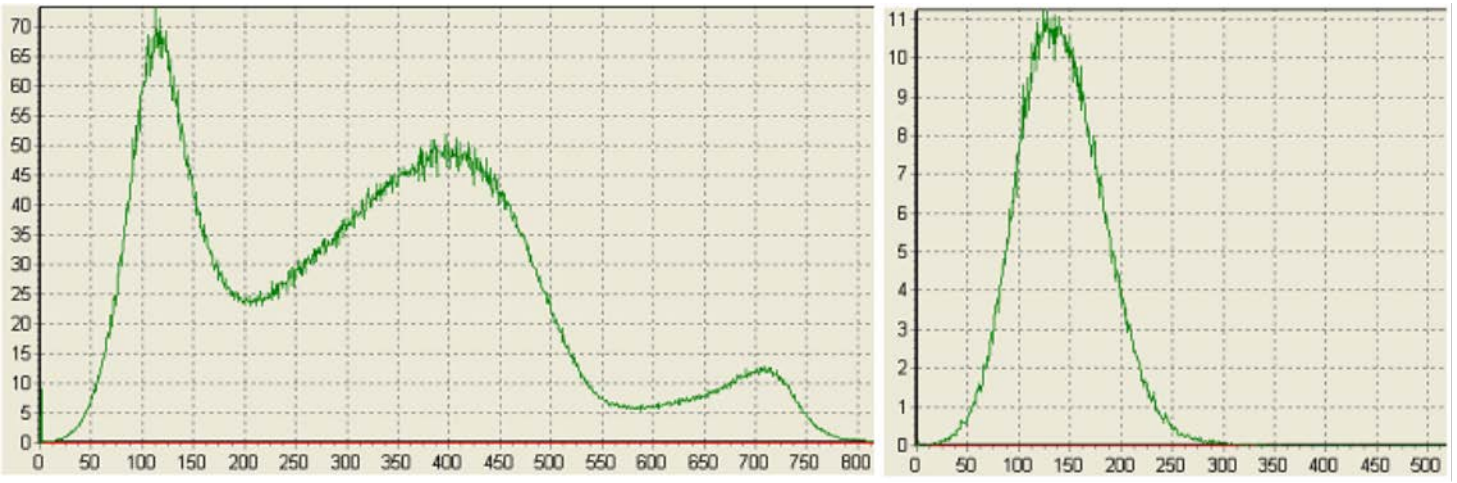


I. Hazan and J. Korkisch; *Anion-exchange separation of iron, cobalt and nickel*



- Acetone anion exchange gave good results, purifying nickel and iron fractions from cobalt and allowing their measurement in LSC.

- Only the first four active samples underwent anion exchange + Ni-resin process. Due to the problems with the separation and the need to add a step for cobalt removal, initial plan was abandoned and the rest of the samples were done with only acetone anion exchange.



BWR Fe sample LSC spectra before and after acetone anion exchange.

Results

- The new method provided good decontamination for both Fe and Ni-fractions.
- Chemical yield was excellent (>90 %) for both metal fractions for BWR samples. For VVER samples Ni recovery was significantly lower.
- Reason for worse recovery of VVER nickel not known (Sample differences, mistake in separation?).

MP-AES measurements for samples with only acetone anion exchange used

Sample	**BWR c**			**BWR d**			**VVER c**			**VVER d**		
Element	**Fe**	**Ni**	**Co**	**Fe**	**Ni**	**Co**	**Fe**	**Ni**	**Co**	**Fe**	**Ni**	**Co**
Initial amount in steel sample (mg)	181,0	3,1	2,1	181,7	3,2	2,2	179,0	2,3	2,0	176,1	2,3	2,0
Recovered amount in Fe-fraction (mg)	168,0	0,0	0,0	174,7	0,0	0,0	158,5	0,0	0,0	162,3	0,0	0,0
Yield (%)	**92,8**	**0,0**	**1,7**	**96,2**	**0,0**	**1,5**	**88,5**	**0,0**	**1,9**	**92,2**	**0,0**	**1,7**
Recovered amount in Ni-fraction (mg)	0,9	3,0	0,0	0,2	2,9	0,0	0,1	0,7	0,0	0,1	1,1	0,0
Yield (%)	**0,5**	**96,8**	**2,0**	**0,1**	**92,4**	**2,0**	**0,0**	**31,2**	**2,1**	**0,0**	**47,8**	**2,2**

Conclusion

- When the amount of iron is very high compared to nickel and cobalt, it starts causing problems with regular anion exchange and nickel resin separations.
- To compensate, the amount of anion exchange resin and nickel resin needs to be increased, making separation process cumbersome and costly.
- Acetone anion exchange gives good results and is cheap and easy. All metals separated in a single process and suitable for larger amounts of iron.
- Needs large amounts of washing solutions and produces high volumes of eluate.

Thank you for listening