R-05-77

Measurements of activity concentrations of ^{59}Ni and ^{63}Ni in spent ion-exchange resins

Final report for SKB project "Ni-59 i jonbytarmassor"

Version 2.0

Per Persson, Lund University

December 2005

Svensk Kärnbränslehantering AB
Swedish Nuclear Fuel
and Waste Management Co
Box 5864
SE-102 40 Stockholm Sweden
Tel 08-459 84 00
+46 8 459 84 00
Fax 08-661 57 19
+46 8 661 57 19

ISSN 1402-3091
SKB Rapport R-05-77

Measurements of activity concentrations of ^{59}Ni and ^{63}Ni in spent ion-exchange resins

Final report for SKB project "Ni-59 i jonbytarmassor"

Version 2.0

Per Persson, Lund University

December 2005

Contents

1 Introduction

This study has been focused on determining the concentrations of ^{59}Ni and ^{63}Ni in spent ion exchange resins from Swedish BWRs and PWRs. The purpose was to be able to perform more reliable calculations on the total amount of ^{59}Ni and ^{63}Ni deposited in the Swedish waste repository SFR.

2 Method

2.1 Sampling and sample description

See reference /Magnusson and Stenström 2005/.

2.2 Sample preparation

Extraction and precipitation of nickel by addition of alcoholic solution of Dimethylglyoxime

1. Filter the remains from the extraction of ^{14}C to get ridge of the ion-exchange resins and other solid material. About 1 g of ion-exchange resins is used for the extraction of ^{14}C. Nickel is released when the acid stripping extracts the inorganic ^{14}C-species.
2. Add approximately 10 mg of tartaric acid ($C_4H_6O_6$). Together with the Fe(III)-ions, the tartaric acid forms complex ions. Preferably, no Fe(III)-ions at all should be present when Dmg precipitates Ni.
3. Add approximately 30 mg of nickel dissolved in concentrated HNO_3. HCl must not be used as in the extraction of ^{14}C some $AgNO_3$ is added and will then form a precipitate of AgCl. (The amount of nickel stuck at the ion-exchange resins is rather small therefore a carrier of stable nickel must be added to be able to extract the active nickel.)
4. Filter, if necessary, the solution to exclude solid material and wash the paper with hot water.
5. Dilute the filtrate with distilled water to a volume of 200 ml in a 400 ml beaker.
6. Neutralise with 2 M NH_3. The colour of the solution darkens.
7. Barely acidify the solution with HNO_3. In an acetous solution, good conditions exist for Dmg to easily form complex ions with Ni as the forming of $Ni(NH_3)_6^{2+}$ is suppressed.
8. Warm the solution to 60–80°C.
9. Add a slight excess of a 1% alcoholic solution of Dmg (25–30 ml), immediately followed by NH_3 until the solution is slightly ammoniacal. Stir well. The forming of $Ni(Dmg)_2$ is facilitated by the adding of NH_3. It takes care of the hydrogen-ions which are created as $Ni(Dmg)_2$ is precipitated as red crystals.
10. Allow the solution to stand on a steam bath for 20–30 min. Stir from time to time.

    Precipitates of porous character absorb a little of the surrounding solution. The Ni-Dmg complex will re-crystallise repeatedly because of the heat. In this process, the precipitate will absorb less and less of the surrounding solution. Also, the process of crystallisation is facilitated because of the heat.
11. Allow the solution to stand at least an hour and cool to room temperature.
12. Filter off the precipitate. Preferably, use a filter pump to speed up the filtering.

    In the filter-crucible, wash the precipitate 6–7 times with 30 ml of distilled water.
13. Dry the precipitate in the filter-crucible at 110–120°C for 45–60 minutes.

14. Transfer the $Ni(Dmg)_2$ (e.g. with a quartz spatula) into a quartz crucible with lid. Combust the precipitate to nickel oxide (Ni(II)O) at 600–800°C. $Ni(Dmg)_2$ will ignite, forming black smoke. Nitric oxides are also formed in the combustion. Continue heating the combusted substance until completely black. The lid of the quartz crucible makes sure that the NiO is not removed from the crucible. A rather violent circulation of gas is created while combusting. A similar situation arises when evaporating the soot from the quartz crucible.
15. In a hydrogen-gas environment, reduce Ni(II)O to metallic Ni at about 800°C.

2.2.1 ^{59}Ni

The metallic nickel is pressed in a copper holder and the sample is ready for measuring. The measurements have been done by detecting the characteristic X-rays (Co k_α) emitted when the ^{59}Ni-nucleus is decaying. The X-rays are measured by a high-resolution germanium detector (Canberra, LEGe GL0210P, active area 200 mm^2, resolution 145 eV FWHM at 5.9 keV). The method has recently been developed in Lund and will be described in a coming report. In order to guarantee the quality of the measurements, a few of the samples where measured with AMS /Persson 2000/, giving the same result.

2.2.2 ^{63}Ni

About 1 mg of the metallic nickel is dissolved in 1.0 ml concentrated HNO_3 in a beaker. The beaker is rinsed with 1.0 ml of distilled water and finally 18 ml of scintillation cocktail (Ultima Gold) is added. The samples are measured by Liquid Scintillation Counting (LSC) (Beckman Coulter LS6500).

2.2.3 Difficulties

It is very important when measuring the samples that they are free from other radionuclides. This is valid both for ^{59}Ni and ^{63}Ni and the mainly disturbing nuclide in both cases is ^{55}Fe but also ^{60}Co can interfere. The sample preparation method described above can be repeated several times but 30–50% of the nickel is lost every time. Even after repeating the preparation method the samples may contain disturbing nuclides. This is the reason why all the subsamples analysed in reference /Magnusson and Stenström 2005/, are not reported here. The measurements did not produce any useful results due to high levels of ^{55}Fe.

3 Results

The results from the analysis of the ^{59}Ni-, ^{63}Ni- and ^{60}Co-measurements of all subsamples possible to measure are presented in Appendix 1. Two of the samples (R-1:5 and R-1:7) were samples from the transparent fraction, i.e. these samples are not representative for the batch sample and therefore not included in the average activities. Further, sample R-1:2, R-1:5 and R-1:6 contained so much ^{55}Fe that the measured values were elevated and not included in the average. In the case of sample R-3:2 and R-4:2, there was not enough nickel left to measure ^{59}Ni, only ^{63}Ni could be analysed. For a few samples no certain value could be determined but in these cases a detection limit is given instead.

Summaries of the results and calculated correlation factors for the analysed spent resin samples are presented in Tables 3-1 to 3-8.

Table 3-1. Summary of the results obtained from PWR reactors in Ringhals.

Sample ID	Reactor	Content	Average ^{59}Ni activity in IX (MBq/kg dw)	Average ^{63}Ni activity in IX (MBq/kg dw)	Average ^{60}Co activity in IX (MBq/kg dw)	Total mass spent IX (kg dw×a^{-1})[1]	Batch sample D.S. content	Total ^{59}Ni activity in spent resins (GBq)	Total ^{63}Ni activity in spent resins (GBq)	Total ^{60}Co activity in spent resins (GBq)
IX 1	R3	CS operation	1.1	179	49.5	440	43%	0.48	78.8	21.8
IX 2	R2	2 years of production	7.0	1,328	234.8	1620	42%	11.3	2,151	380
IX 3	R4	CS shut down, spent fuel pool, waste processing	10.6	1,013	167.7	1,150	43%	12.2	1,165	193
IX 4	R3	CS shut down, spent fuel pool, waste processing	2.0	282	114.4	2,060	43%	4.1	581	236

[1] Total mass dw calculated based on a D.S. content of 45%.

Table 3-2. Calculated correlation factors for the analysed spent resin samples from PWR reactors.

Sample ID	Reactor	Content	Total ^{59}Ni activity in spent resins (GBq)	Total ^{63}Ni activity in spent resins (GBq)	Total ^{60}Co activity in spent resins (GBq)	^{59}Ni/^{60}Co	^{63}Ni/^{60}Co	^{59}Ni/^{63}Ni
IX 1+ 4	R3	CS shut down, spent fuel pool, waste processing	4.58	659.8	258	0.018	2.55	0.0069
IX 2	R2	2 years of production	11.3	2,151	380	0.029	5.66	0.0053
IX 3	R4	CS shut down, spent fuel pool, waste processing	12.2	1,165	193	0.063	6.04	0.010

Table 3-3. Summary of the results obtained from BWR-HWC reactors.

Sample ID	Reactor	System	Average ^{59}Ni activity in IX (MBq/kg dw)	Average ^{63}Ni activity in IX (MBq/kg dw)	Average ^{60}Co activity in IX (MBq/kg dw)	Total mass spent IX (kg dw×a^{-1})[2]	Batch sample D.S. content	Total ^{59}Ni activity in spent resins (GBq)	Total ^{63}Ni activity in spent resins (GBq)	Total ^{60}Co activity in spent resins (GBq)
IX 1	B2	332	0.019	0.92	12.6	5,190	37%	0.099	4.77	65.4
IX 2	B2	332	0.017	0.53	7.1	5,190	47%	0.088	2.75	36.8
IX 3	O1+O2	324	0.17	21.6	2,338	239	37%	0.041	5.16	559
IX 4	B2	331+ 342	0.044	4.4	286	1,500	36%	0.066	6.60	429
							Total	0.29	19.3	1,090

[2] Total mass dw calculated based on a D.S. content of 45%.

Table 3-4. Calculated correlation factors for the analysed spent resin samples from BWR-HWC reactors.

Sample ID	Reactor	System	^{59}Ni/^{60}Co	^{63}Ni/^{60}Co	^{59}Ni/^{63}Ni
IX 1	B2	332	1.51E–3	0.073	0.021
IX 2	B2	332	2.39E–3	0.075	0.032
IX 3	O1+O2	324	7.33E–5	0.0092	0.0079
IX 4	B2	331+ 342	1.54E–4	0.015	0.010

Table 3-5. Calculated correlation factors for the total activity for the analysed spent resin samples from BWR-HWC reactors.

Total ^{59}Ni /total ^{60}Co	Total ^{63}Ni /total ^{60}Co	Total ^{59}Ni /total ^{63}Ni
2.7E–4	0.018	0.015

Table 3-6. Summary of the results obtained from BWR-NWC reactors.

Sample ID	Reactor	System	Average ^{59}Ni activity in IX (MBq/kg dw)	Average ^{63}Ni activity in IX (MBq/kg dw)	Average ^{60}Co activity in IX (MBq/kg dw)	Total mass spent IX (kg dw·a^{-1})[3]	Batch sample D.S. content	Total ^{59}Ni activity in spent resins (GBq)	Total ^{63}Ni activity in spent resins (GBq)	Total ^{60}Co activity in spent resins (GBq)
IX 1	F1+F2+F3	331	0.354	31.4	250	3,010	44%	1.07	94.5	753
IX 2	F1+F2+F3	332	0.14		22.3	13,400	35%	1.88	67.0	299
IX 3	F1+F2+F3	324	0.057	8.29	17.1	790	35%	0.045	6.55	14
IX 4	F1+F3	342	0.22	49.4	282	3,620	39%	0.80	179	1,021
							Total	3.8	347	2,087

[3] Total mass dw calculated based on a D.S. content of 45%.

Table 3-7. Calculated correlation factors for the analysed spent resin samples from BWR-NWC reactors.

Sample ID	Reactor	System	$^{59}Ni/^{60}Co$	$^{63}Ni/^{60}Co$	$^{59}Ni/^{63}Ni$
IX 1	F1+F2+F3	331	1.42E–3	0.13	0.011
IX 2	F1+F2+F3	332	6.29E–3	0.22	0.028
IX 3	F1+F2+F3	324	3.21E–3	0.47	0.0069
IX 4	F1+F3	342	7.84E–4	0.18	0.0045

Table 3-8. Calculated correlation factors for the total activity for the analysed spent resin samples from BWR-NWC reactors.

Total ^{59}Ni /total ^{60}Co	Total ^{63}Ni /total ^{60}Co	Total ^{59}Ni /total ^{63}Ni
0.0018	0.17	0.011

4 Discussion and conclusion

The total ^{59}Ni and ^{63}Ni activities in spent resins produced annually from each reactor unit can be estimated based on the above results. The simple model used is:

B1=B2
B2=(IX 1+IX 2)/2 + IX 3 + IX4 from Table 3-3.
O2=B2
R1=B2*25,00/1,800
R2=R2
R3=R3
R4=R4
Forsmark = sum of the results in Table 3-6.
O1+O3=B2*5,000/1,800

B1, B2 and O2 all have the same thermal power and operate with HWC; accordingly, they are assumed to have the same production of Ni-isotopes. The production in R1 is scaled from B2 by their thermal powers.

The larger amounts of Ni in the resins from Forsmark compared to Barsebäck 2 may be explained by use of carboxylate cation exchangers in the condensate clean-up system (332) in Forsmark units 1 and 2. This resin is less acidic than the sulfonte cation exchangers used in the other BWR-plants. The Forsmark resins cannot retain the amines released from the degradation of the anion resin; in the other BWR-plants they are retained. When the amines arrive in the reactor coolant, they are radiolyzed into nitric acid, which lowers the pH and increases the solubility of Ni. This means that there will be a higher uptake of Ni on the resins in the reactor coolant clean-up system (331) and in the waste treatment resins (342). In addition, the higher moist contents of the steam in Forsmark units 1 and 2, compared to Barsebäck 2, leads to a larger amount of Ni in the condensate clean-up resins (332).

The Forsmark units and O1+O3 operate with NWC; despite this, the production in O1+O3 is scaled from B2 according to their thermal powers. The reason for this is the discussion above on the chemistry conditions in Forsmark units 1 and 2 (Lundgren 2005 and Aronsson 2005, personal communication).

Table 4-1. The total ^{59}Ni and ^{63}Ni activities in spent resins produced annually.

	^{59}Ni (GBq)	^{63}Ni (GBq)
B1	0.20	15.5
B2	0.20	15.5
O2	0.20	15.5
R1	0.28	21.6
R2	5.65	1,075
R3	4.58	660
R4	12.2	1,165
Forsmark	3.8	347
O1+O3	0.56	43.1
Sum	27.7	3,358

Based on the data presented in Table 4-1, the total ^{59}Ni and ^{63}Ni activities in spent resins generated during the life time of the reactors has been calculated. This corresponds to the total theoretical amount of ^{59}Ni and ^{63}Ni in spent resins that will be – or has been – deposited in the Swedish waste repository SFR. The calculations assume a reactor life time of 40 years (except for B1 and B2, where the actual life times of 24 and 28 years, respectively, have been used). The results are presented in Table 4-2.

In the results presented in this report no uncertainties have been given but a realistic estimation is about 30% both for ^{59}Ni and ^{63}Ni. The major part of the uncertainties depends on the sample collection; the spent ion exchange resins are not homogeneous.

Table 4-2. The total ^{59}Ni and ^{63}Ni activities in spent resins produced during the life time of the reactors.

	^{59}Ni (GBq)	^{63}Ni (GBq)
B1	4.8	372
B2	5.6	435
O2	8	621
R1	11.1	862
R2	226	43,000
R3	183	26,400
R4	488	46,600
Forsmark	152	13,880
O1+O3	22.2	1,724
Total	1,100	134,000

5 References

Magnusson Å, Stenström K 2005. “^{14}C produced in Swedish nuclear power reactors – Measurements on spent ion exchange resins, various process water systems and ejector off-gas ”, Internal Report LUNFD6/(NFFR-3098)/1-33/(2005), Lund University.

Persson P et al. 2000. “Determination of the detection limit of ^{59}Ni at the Lund AMS facility by using characteristic projectile X-rays”NIM B 160 (2000) 510-514.

Appendix 1

Measured values of concentrations of ^{59}Ni and ^{63}Ni in spent resin sample

Sample	Added Ni (mg)	Jonb (g)	^{59}Ni (MBq/kg ww)	^{63}Ni (MBq/kg ww)	^{60}Co (MBq/kg ww)
R-1:2	35.2	1.695	0.604	151	21.3
R-1:5	33.6	1.024	0.246	53	21.3
R-1:6	28.3	1.2693	0.603	82	21.3
R-1:7	31.2	1.1888	0.037	8	21.3
R-1:8	29	1.3075	0.236	77	21.3
R-2:1	30.5	1.672	2.293	590	98.6
R-2:2	26.5	1.055	3.453	367	98.6
R-2:6	27	1.077	3.118	716	98.6
R-3:1	36.8	1.179	3.993	426	72.1
R-3:2	28.1	1.137		403	72.1
R-3:4	27.2	1.325	5.109	478	72.1
R-4:2	24.7	1.582		149	49.2
R-4:3	27	1.489	1.026	92	49.2
R-4:4	26	1.723	0.664	123	49.2
B-1:2	33.4	1.2494	< 0.007	0.34	4.68
B-2:2	28	0.983	< 0.008	0.25	3.33
B-3:2	37.4	1.7849	0.063	8	865
B-4:2	23.8	1.0957	0.016	1.6	103
F-1:1	28	1.0068	0.156	13.8	110
F-2:1	42.5	1.4608	< 0.05	< 5	7.8
F-3:2	29	1.22	0.020	2.9	6.0
F-4:1	37.7	1.329	0.049	5.0	110
F-4:2	46.8	1.338	0.127	33.5	110