Resin intrusion into the primary circuit of NPP Jaslovske Bohunice V-1.

Ing.Ondrej Grežďo, SE a.s, grezdo.ondrej@ebo.seas.sk
Ing. Mráz Viliam, SE a.s, mraz.viliam@ebo.seas.sk

INTRODUCTION

During the 1st unit core loading on the 17th April 2005 operational personnel detected a silt of dirt on the vertical part of the rack for spent fuel in the spent fuel pond. Later the dirt was identified as a ion exchange resin used in purification systems on the NPP V-1 units.

The core loading was interrupted and the accident commission decided to discharge all fuel from the core to the spent fuel pond. Because experts were not able to determine positively consequences of resin existence in the primary circuit, expert commission made decision that the primary circuit, fuel assemblies and auxiliary system have to be cleaned. The special program was implemented for control all accessible parts of the primary circuit, safety systems and other auxiliary systems. Resin was found in most of the fuel assemblies, pipes and tanks in the primary circuit and his auxiliary system. Location of the ion exchangers was identified in the systems by standard diagnostic equipment in NPP and by special equipment of a company ALLDECO.

BEHAVIOUR OF THE ION EXCHANGER (RESIN) IN THE PRIMARY CIRCUIT

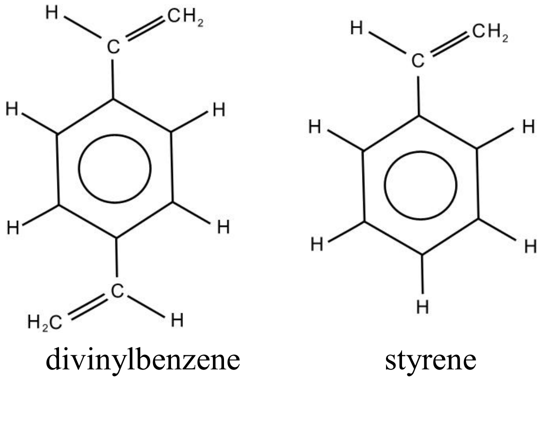
There is only a few information about behaviour of the ion exchanger (resin) in the primary circuit because conditions in the primary circuit (pressure, temperature, radiation) are difficult simulated. Most of available information is from real events on working units.

Ion exchanger (resin) penetrated to the primary circuit on several units - Fessenheim, Nord, Kola, Duane Arnold, Dungennes B.

Information about behaviour of the ion exchanger (resin):

1. Resin skeleton material is the styrene and the divinylbenzene copolymer. There are these functional groups embedded on the skeleton:
    - anion exchange resin - trimethylammonium
    - cation exchange resin - sulphonic acid

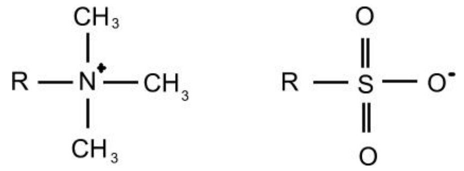
Fig.1 Skeleton material



divinylbenzene styrene

Fig.2. Functional groups

trimethyl R-amin sulphonic acid ion



2. When the temperature increases above operational limits (60-80°C cation resin, 40-60 °C anion) resin decompose progressively.

   The decompose products are:

   - **Sulphates, nitrates , ammonium** Increased concentration of sulphate may cause local rust in the some types of austenitic steel. Acid anion production decreases pH parameter. Low pH supports the corrosion and the corrosion products transport.
   - **Methane , ethane, polyvinyl group , carbonic acid, acetic acid , formic acid** -This products increase hydrogen and TOC(Total Organic Carbon) concentration in the primary circuit coolant. Dozens of litre resin leakage in the PWR reactor caused hydrogen concentration increase up to 15 mg/l. Decompose products may cause the opacity of coolant.

3. From the point of view of mechanical quality the ion exchanger becomes darker and harder by increasing temperature and may cause erosion of the fuel cladding and the primary circuit. Erosion is indicated by increase of concentration and activity of the corrosion products.
4. It is possible that the ion exchanger soften, however there is not enough experimental data. It is more probable that the ion exchanger in association with suspended corrosion products can create sediment in the narrow part (grid of rod fuel, etc.)

AFFECT OF EVENT ON THE NUCLEAR SAFETY

Event had not direct affect on nuclear safety of the unit. The primary circuit was infiltrated by the ion exchanger during outage of unit. Before the core loading was repeated operator analysed and identified possible risks of operation on the 1st and the 2nd unit:

- Potential (possible) stuck of control rod in the top position. Blocking spaces with narrowed section - influence on rod mobility and rod drop time.
- Potential damage of bearings of main circulation pump, plugging of auxiliary circuit of main circulation pump
- Potential influence on measurements by reason of plugging measurement lines
- Potential increase of radiation exposure along primary circuit loops.
- Potential decrease of reactor flow because of aggradation by ion exchanger in fuel rods

- Potential wearing of fuel rods with sintered ion exchanger and then risk of dehermetization of fuel cladding.
- Potential increase of concentration of hydrogen in reactor coolant
- Potential increase of concentration of sulphates and organic acids in reactor coolant -risk of rust austenitic materials
- Potential increase of corrosion products concentration in the primary circuit - risk of fix on fuel clad

FINDING OF THE ION EXCHANGER SOURCE

After detection of the ion exchange resin in reactor and spent fuel pond, samples were taken from various parts of primary circuit and tested for searching ion exchanger sources.

Types of analysis:

1. Visual comparison by optical and electron microscope
    - Search was unproductive because copolymer structure is amorphous. Internal grindings steamed with gold without differences too.
    - Diameter of pellets is 0,5 - 0,7 mm. The number is several millions pellets per litre.
    - Resin producer confirmed that it is difficult to recognise the ion exchanger visually.
2. Gama-spectrometric measurement
    - eliminated some types of the ion exchanger because of too low activity
    - wide range of activity was detected in the spent fuel pond
    - results could be biased because the ion exchanger maybe saturated
3. RTG probe, LIBS spectrometry
    - goal is distinction of anion and cation exchange resin.
    - RTG probe, LIBS spectrometry did not established nitrogen in anion exchanger. Sulphur did established in cation exchanger.
    - After saturation by hydrochloride acid anion exchanger was recognized

Results

- Identification of unknown ion exchanger is very difficult. There was analysed single pellets of ion exchanger, it means the weight of results is minimal because primary circuit contains several million pellets of ion exchanger.
- Measured wide range of parameters - activity, content of sulphur and chlorine indicates mixture of ion exchangers with different types and ages.

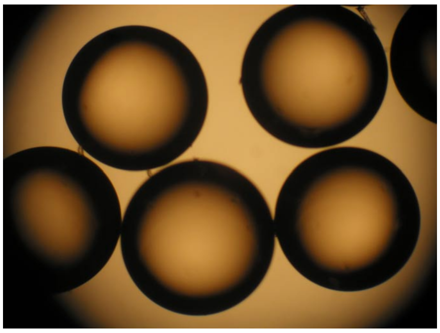


Fig.3.Amberlite IRN77 fresh cation resin

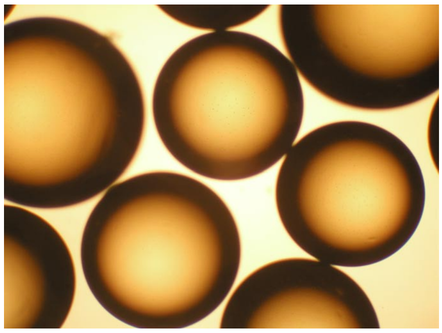


Fig.4.Amberlite IRN78 fresh anion resin

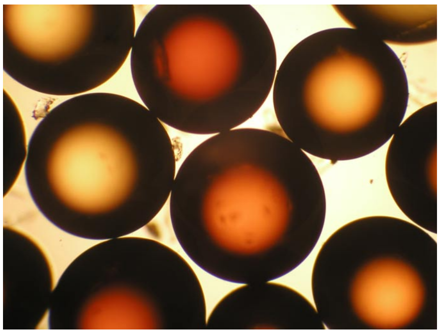


Fig.5. Resin from spent fuel pond

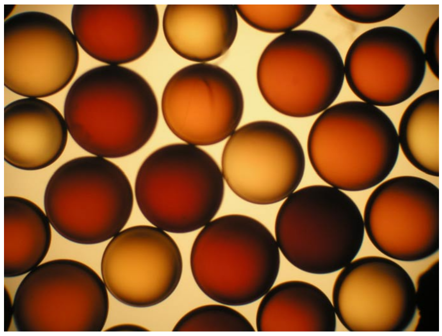


Fig.6. Resin from reactor vessel

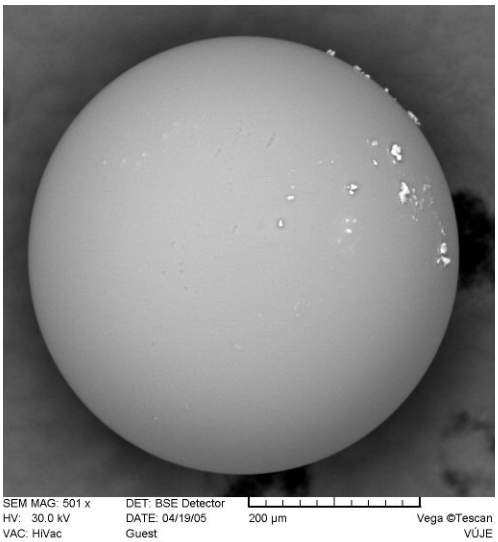


Fig.7. Enlarged Amberlite IRN77

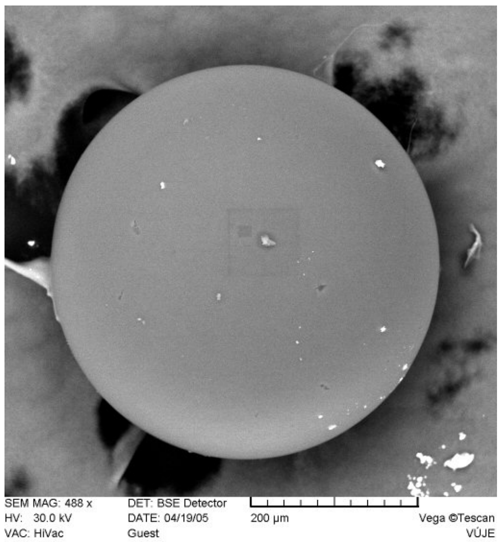


Fig.7 Enlarged Amberlite IRN78

CLEANING OF THE PRIMARY CIRCUIT AND FUEL ASSEMBLIES

There were identified places with ion exchanger in technology systems of unit by standard diagnostic equipment of NPP and by special equipment of company ALLDECO. Later on there was realised cleaning of all spaces and systems contaminated by the ion exchange resin. The goal was to complete cleaning the primary circuit - to remove the ion exchanger.

The following systems were cleaned:

- All loops were flushed by demineralised water to the reactor vessel.
- Pressure control system was flushed by demineralised water to the reactor vessel.
- Hydraulic part of main circulation pump including their auxiliary circuits
- Core barrel and core basket
- Bottom of the reactor vessel
- Pipelines of the emergency core cooling system (ECCS)
- ECCS tank HD10N-1
- Reactor spray system
- The chemical and volume control system including tank ND 10 N-1
- Tanks CD30N-1(dreinage tank) a RB40N-1(boron acid solution tank)
- Lines HD30Č-1 a BA20Č-1
- Spent fuel pond
- All fuel assemblies were cleaned in KHP (equipment for fuel tightness control)
- Additional cleaning of coolant before start-up in blow-down water purification system SWP-1

Table 1. Ion exchanger(resin) approximation balance

Section	Lost [l]	Found [l]
Spent fuel pond	-	unspecified
Fuel assemblies	-	0.1
Reactor vesel	-	unspecified
Primary circuit	-	
ALLDECO+EBO		
LOOP .N 1	-	10.1
LOOP .N 2	-	3.1
LOOP .N 3	-	1.1
LOOP .N 4	-	0.1
LOOP .N 5	-	4.1
LOOP .N 6	-	15.1
SWP-2	cca 1000	-
CD30N -1	-	3000
CD30 N -2	-	unspecified
HD10N-1 :	-	
- clean part	-	10
- dirty part	-	50
SWP-4	cca 2800	-
Total	cca 3800	cca 3190

REASONS

Immediate reason of this failure is leakage of ion exchanger trap of cooling pond and ECCS tank water purification system (SWP-4). Reason of huge contamination of technology with ion exchanger is movement of great water capacity because of ECCS tank was cleaned.

Root reasons of penetration of ion exchange resin to technology are:

- Insufficient monitoring of contents of the filters
- Insufficient monitoring of dirt in tanks
- Missing remedies after finding ion exchanger in ECCS tank in the past
- Ineffective acceptance practice from WANO

OPERATIONAL CONTROL AFTER CLEANING OF TECHNOLOGY

Chemical analysis of water purity of the primary circuit

Common (hydrogen, corrosion products) and special (methane, sulphates, acetic acid) parameters monitoring of chemical regime did not exceed standard level.

Table 2.Start-up chemical monitoring measurements

Date	Hydrogen [Nml/kg]	Sulphates [μg/kg]	Methane [μg/kg]	Acetic [μg/kg]	Fe [μg/kg]	Co-58 [kBq/kg]	Co-60 [kBq/kg]	Mn-54 [kBq/kg]
1.6.2005		495		14	381,1	1411,7	568,5	873,8
2.6.2005		217		<1	587,6	124,0	18,1	27,5
3.6.2005		143		64	26,4	38,8	18,0	25,9
4.6.2005		154		78	46,8	1974,1	1113,9	1540,1
5.6.2005		167		317	29,5	13,4	3,1	5,9
6.6.2005	12	96	77	435	11,4	5,0	1,4	3,5
7.6.2005	13	19	120	256	4,8	5,5	2,12	4,26
8.6.2005	31	13	89	60	15,8	17,8	8,6	14,9
9.6.2005	42	<1	73	52	33,4	6,0	1,9	1,9
10.6.2005	34	<1	68	40	25,2	7,6	2,26	2,5
11.6.2005		<1		27		25,1	6,8	12,6
12.6.2005		<1		106		183,7	44,6	78,0
13.6.2005	45	<1	325	370		7,5	<5,6	<5,9
14.6.2005	41	<1	377	375		6	1,6	2
15.6.2005	39	<1	608	509		20,1	5,2	7,7
16.6.2005	36	<1	780	295		3,6	1,5	2
17.6.2005	40	<1	790	261	9,1			
20.6.2005	46	<1	620	157				
21.6.2005	48	<1	630	173				
24.6.2005	43	<1	490	187	2,4	3,9	1,6	2

Date	Hydrogen [Nml/kg]	Sulphates [µg/kg]	Methane [µg/kg]	Acetic [µg/kg]	Fe [µg/kg]	Co-58 [kBq/kg]	Co-60 [kBq/kg]	Mn-54 [kBq/kg]
28.6.2005	47	<1	440	170				
01.7.05	45	<1		556	8,9			
08.7.05	50	<1		317	1,2			
12.7.05	49	<1		155				
15.7.05	52	<1		127	?			
19.7.05	46	<1	480	115				
22.7.05	?	<1	?	113	?			

The result of chemical monitoring of coolant showed that the amount of the ion exchanger in the primary circuit does not influence the quality of coolant water.

Hydraulic analysis of the primary circuit

The goal of this measurement is to prove the stability of hydraulic parameters of the primary circuit. 43 measurements were executed:

- 12 measurements in cold state (coolant temperature 41 - 47^{o}C)
- 7 measurements during coolant water heating (coolant temperature 50 - 200^{o}C)
- 12 measurements during physical start-up (coolant temperature 245 - 260^{o}C)
- 12 measurements on power levels 55, 70 a 100 % nominal power and after 30 days on 100 % nominal power (273-280^{o}C)

The result of hydraulic analysis of the primary circuit showed that hydraulic parameters of the primary circuit are stable.

Power distribution

Target was the monitoring of the outlet temperature and the power distribution of fuel assemblies every 20 effective days. Differences were not detected between measurements and calculations of power distribution.

Control rod mobility

Target was the verifying of control rods mobility in all scale of the core height. The measurement was realised 60 days after the start of the campaign. Control rods are movable in all scale of height. No anomalies were noticed.

Rod drop time

Target was to verify rod drop time at interval 8 - 13 second. Measurement was realised 60 days after the start of the campaign. Drop time of all control rods is at interval 8 - 13 sec.

CONCLUSION

The cleaning technology of the primary circuit and all fuel assemblies prolonged the outage of the 1st unit by 30 days. Loss of electricity production was 329 007 MWh. The resin existence in the primary circuit have not been established up to the moment.

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