



## WATER CHEMISTRY IN WWER REACTORS

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### Abstract

In this paper "Water Chemistry in WWER Reactors", are briefly described the 30 WWERs in Russia and the Ukraine, and are pointed out the essential differences between the 440s and 1000s. The primary coolant in the six loops of the former type operates at 270 - 290 °C, while the four loops of the latter type are at 290 - 320 °C.

Performance of the fuel has been generally good with some fission product activities emanating from tramp uranium. Incidents causing unusually high fission product levels were overheating of the 16th fuel load at Kola NPP in 1990 by a reduced coolant flow, and fuel defects at Novovoronezh NPP resulting from deposits of carbon and corrosion products. Organic carbon, depositing from the coolant in regions of high turbulence (i.e. at the spacer grids), provokes corrosion product deposition. The source of the organic is not known.

New chemistry guidelines have been implemented since 1992 - 93 for Russian and Ukrainian WWERs. These include higher  $\text{pH}_T$  values (7.0 - 7.1 as opposed to 6.6 - 6.9) and tighter controls on oxygen and impurities. Lower dose rates in steam generator channels are reported. Significant reduction in operator doses are achieved by these methods coupled with a "soft decontamination" involving changing the KOH concentration and, hence, the  $\text{pH}_T$  before shutdown. The benefits of hydrazine treatment for deoxygenating feedwater and coolant prior to start up, for injecting before shutdown and for general chemistry control on radiation fields are described.

At present, 13 WWER-type reactors are in operation in Russia and 12 in Ukraine. In this amount 8 are the WWER-440 reactors and 17 are the WWER-1000 reactors. Recently unit 4 at Balakovo NPS with WWER-1000 reactor was put into operation.

There are some essential differences between parameters of primary circuit NPS with WWER-440 and WWER-1000 reactors. WWER-440 and WWER-1000 primary coolant circuit include 6 and 4 loops respectively. The coolant temperature ranges is about 270-290 C and 290-320 C in WWER-440 and WWER-1000 primary circuits respectively. The coolant pressure is about 12 and 16 MPa in WWER-440 and WWER-1000 primary circuits respectively.

The most essential differences between reactor blowdown cleaning systems include using ion-exchange and high-temperature filters. All NPS with WWER-440 reactor and WWER-1000 reactors at unit 5 New-Voronezh NPS, unit 1 and 2 South-Ukraine NPS, unit 1 and 2 Kalinin NPS are equipped with mixed bed demineralizers. WWER-1000 reactors at units 1-5 Zaporozhe NPS, units 1-4 Balakovo, unit 3 South-Ukraine NPS, unit 3 Rovno NPS and unit 1 Khmel'nitsk NPS are equipped with high-temperature filters. The mixed bed demineralizer flow is 20 and 30 m<sup>3</sup>/h at WWER-440 and WWER-1000 reactors blowdown cleaning systems respectively. The nominal capacity of a high-temperature blowdown cleaning systems is 400 m<sup>3</sup>/h. The high-temperature filter nominal capacity of each main reactor recirculation loop is equal to 100 m<sup>3</sup>/h.

A correct analysis of fuel cladding reliability of different WWER NPS requires certain factors to be taken into account, such as the fuel burnup level, pre-startup thermal-mechanical and startup chemistry treatments for the surface, the operational and the shutdown water chemistry.

No one failed fuel assembly caused exceeding was in Russian NPPs both in 1991 and 1992 life times. I-131 and I-134 maximum activities in Balakovo NPS unit 1, Kalinin NPS unit 2, South Ukraine unit 2 and 3 were lower level which determined by manufacturing uranium dirt on the fuel rod cladding surfaces only. It means failure clads absence in cores.

Inspections of fuel integrity (IFI) for Balakovo NPS unit 3 was performed after reactor shutdown, using container which placed into the cooling pond. This method include fission products activities measurement to detect a leaking assemblies. Only one fuel assembly was found. Fission products specific activities anomaly raised in the next lifetime beginning.

During Kalinin-1 refuelling in December 1991 2 from 66 fuel assemblies were controlled. 2 FA detected as failure and disposed. A burst activity effluent shows some defected assemblies were resided. All kinds of radioactive impurities deposited then at the primary circuit internal surfaces.

In 1990 during the operation of the 16th fuel load of WWER-440 reactor (60 effective days) at Kola NPP, Unit 2, overheating of practically all the fuel assemblies (FA) of the third year of operation was detected. It was caused by coolant flow rate decrease (20-30%) in the FA. When this fact was revealed unit power was reduced up to 90% nominal power. After 90 Effective days of operation reactor was shutdown to refuelling. during the 17th campaign the condition of the mentioned FA has not changed and after operation during 142 effective days at 90% nominal power, reactor was shutdown.

Inspections of fuel integrity of 317 FA after 15 campaigns revealed 5 leaky fuel assemblies, after 17 campaigns - 3 leaky FA. During 16-17 campaigns specific total primary coolant activity (by the sum of iodine radionuclides) fluctuated within the limits of 0.17-0.59 mCi/kg, which is one order of magnitude higher than the coolant activity level of the Kola NPP other units.

Out-of-core inspections of the mentioned fuel assemblies in the Novovoronezh NPP hot cell revealed deposits on the fuel rod surfaces, having filled the gaps between fuel rods and spacer grids. Maximum amount of deposits with the thickness of up to 1mm, is on the peripheral fuel rods (FRs) in the zone of spacer grids 1 and 2 (from the low part of the fuel bundle) with damages in grids 1,2 and 3. There are through-wall defects in some fuel rods. Chemical and spectral analysis showed that the composition of deposits includes carbon, as well as corrosion products of circuits and fuel rods (Fe, Cr, Ni, Co, Mn, Zr etc.), and also carbon and iron are the main elements (by mass). Inspection results allowed to suggest that the cause of the mentioned event is the deposition of organic compounds from the coolant into the zones with the high flow turbulence (spacer grids). These deposits are the base for structural materials corrosion products precipitation from the coolant flow. The cause of the organic elements appearance in the WWER-440 primary circuit coolant of the Kola NPP is not clear enough.

To evaluate influence of water chemistry on fuel cladding behaviour All-Russian Scientific Research Institute of Nuclear Power Plants has carried out an analysis of data from fuel cladding failures and chemistry monitoring operations on nuclear power-generating units with water-moderated water-cooled (WWER) reactors. Data base include the results of statistical processing of operation data on chemical monitoring of the primary coolant in power-generating units operating with WWER-1000 and WWER-440 reactors. Analysis of the data base obtained makes it possible to compare both the conduct of chemical treatment over a working campaign for power-generating units with WWER reactors on different NPS.

Standard combined ammonia-potassium, hydrazine-potassium and mixed hydrazine-ammonia-potassium water treatment with regulation by boric acid is used in the primary loop of different units NPS with WWER reactors.

The concept of water chemistry ensures that pHt values and hydrogen concentration corresponding to positive values of the temperature gradient of magnetite solubility near its minimum are retained through the working campaign. According to the concept of water chemistry, the fulfilling of this conditions should lead to minimizing of corrosion product deposits in the fuel cladding.

Statistical processing of chemical monitoring data shows that in period before 1992 the mean pHt value was 6.6-6.9 over the whole working campaign. The water chemistry WWER reactor recent guideline ensures that pHt values correspond not to a constant pHt level, but to a variable one, with a monotonic increase over a working campaign constituting on average around 6.7 for WWER-1000 and 6.8 for WWER-440 reactors.

At 1992-1993 in Russian and Ukrainian, NPS with WWER reactors were implemented new the water chemistry guideline. This correction guarantee the possibility of carrying out water treatment with a constant pHt value at level about 7.0-7.1 at in-let reactor temperature (270 and 290 °C at WWER-440 and WWER-1000 respectively).

With revision of primary circuit water chemistry standards:

- controls are in place on Russian and Ukrainian NPS for radiochemical monitoring of radionuclides corrosive origin in the coolant (Cr-51, Co-60, Co-58, Mn-54, Mn-56 and Fe-59),
- maximum admissible concentration of oxygen in the coolant as been reduced from 0.01 to 0.005 ppb,
- the alkali metals (K + Li + Na) - boric acid concentrations mode of operation as been corrected.

As a result of the letter, there has been pHt value increase in the working campaign beginning and reduction at the end.

The alkali metal - boric acid mode of operation for WWER-440 and WWER-1000 before and after revision of standards in 1992-1993 is shown in Fig. 1 and 2. Constant pHt lines correspond calculated ammonia concentration 15 ppm and the in-let reactor coolant temperature (270 and 290 °C at WWER-440 and WWER-1000).

WWER reactors use a mixed ammonia-potassium (NH<sub>3</sub>-K) water chemistry with hydrogen produced by radiolysis of ammonia or hydrazine. The most essential differences between primary water chemistry of WWER reactors include pHt and hydrogen concentration levels of operation.

Mean values and variation ranges in main coolant quality characteristics in first loop of Russian and Ukrainian NPP with WWER-440 and WWER-1000 in 1990-1992 is shown in Table 1-6. Information processing include determination both of standard deviation from mean value and proportion of time norm observed for a hydrogen and a total alkali metal concentrations.

Dosage levels for staff and associate workers on Russian and Ukrainian nuclear power stations with WWER reactors at 1990-1992 is shown in Table 1-6 and Fig. 3-4. Handling data include determination of mean individual dose, collective dose and standardized exposure levels. Operating water chemistry and dosage exposure data of Russian and Ukrainian NPP before 1990 were published earlier.

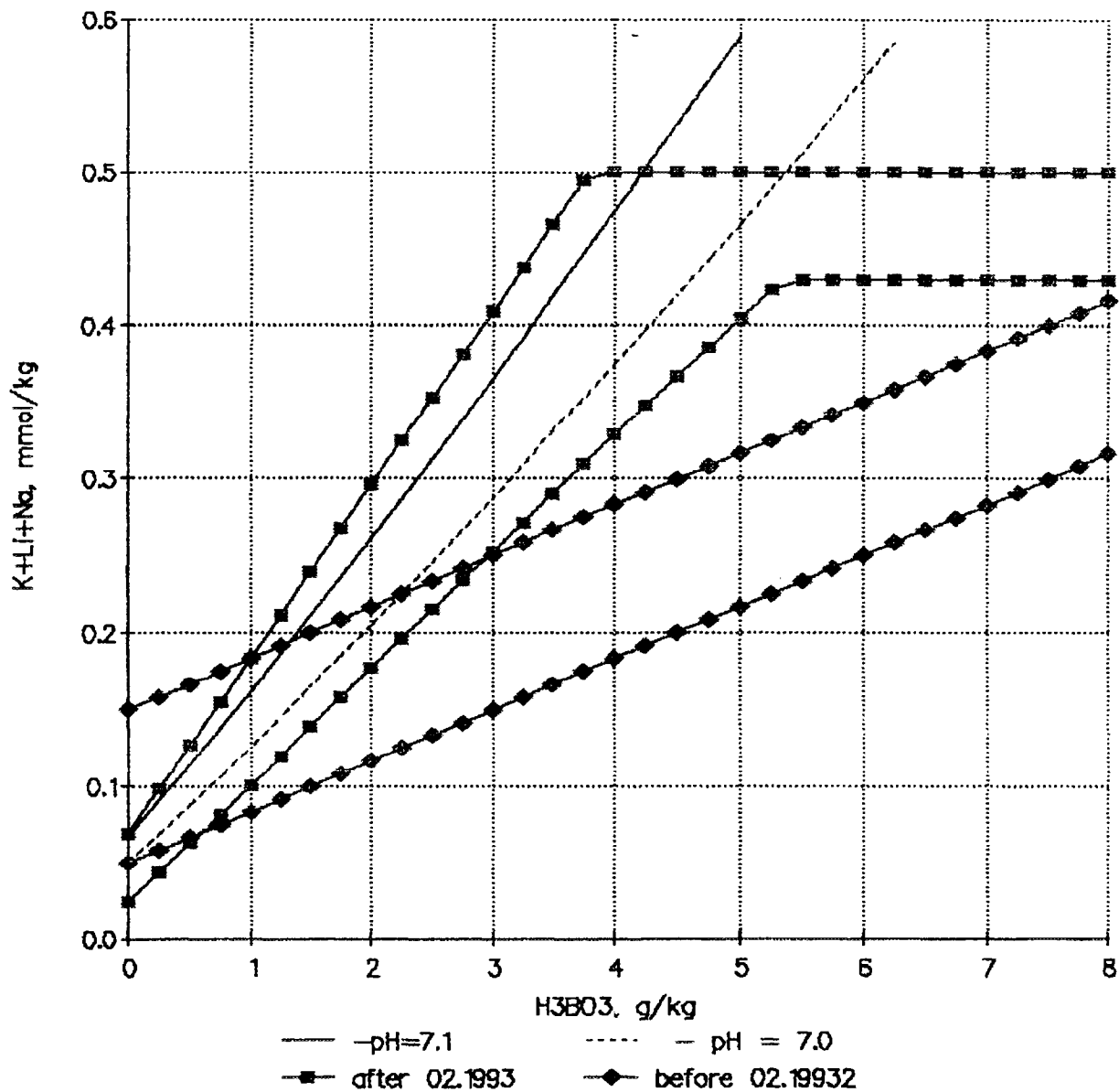


FIG. 1 WWER-440  $pH_{270}$  ( $NH_3=15$  ppm)

Comparison of primary circuit water chemistry during 5th and 6th fuel lifetime at unit 3 Zaporozhe NPS showed both stabilization and increase pH value (see Fig. 5-6). As a result a dose rate reduction in steam generator channel were observed.

Primary circuit water chemistry instability during 5th fuel lifetime at unit 2 Balakovo NPS cause a radiation situation deterioration.

Primary circuit water chemistry was variable from first to seventh fuel lifetime at Kalinin NPS unit 1 and from first to fifth fuel lifetime at unit 2 Kalinin NPS unit 2.

A soft decontamination of primary circuits were realized initially in 1985 at NPS Novovoronezh unit 5 (WWER-1000 reactor). In 1993 the primary circuit soft decontaminations were realized at NPS Kalinin unit 2, NPS South Ukraine unit 1 and 2. An experience accumulated allow to propose that correctly manipulated water chemistry during reactor shutdown ensure a significant dose rate reduction

in maintenance and refuelling. Doserates are caused either by radiation of radionuclides carried by the water or by radionuclides deposited at the internal surfaces of primary circuit equipment.

A corrosion radionuclides dynamics in primary coolant during Kalinin NPS unit 2 reactor shutdown 1992 is shown in Fig 7-9. A primary coolant and cleaned water after mixed bed demineralizers and H-cation filters were controlled. Maximum in corrosion product activities corresponds to boric acid increase.

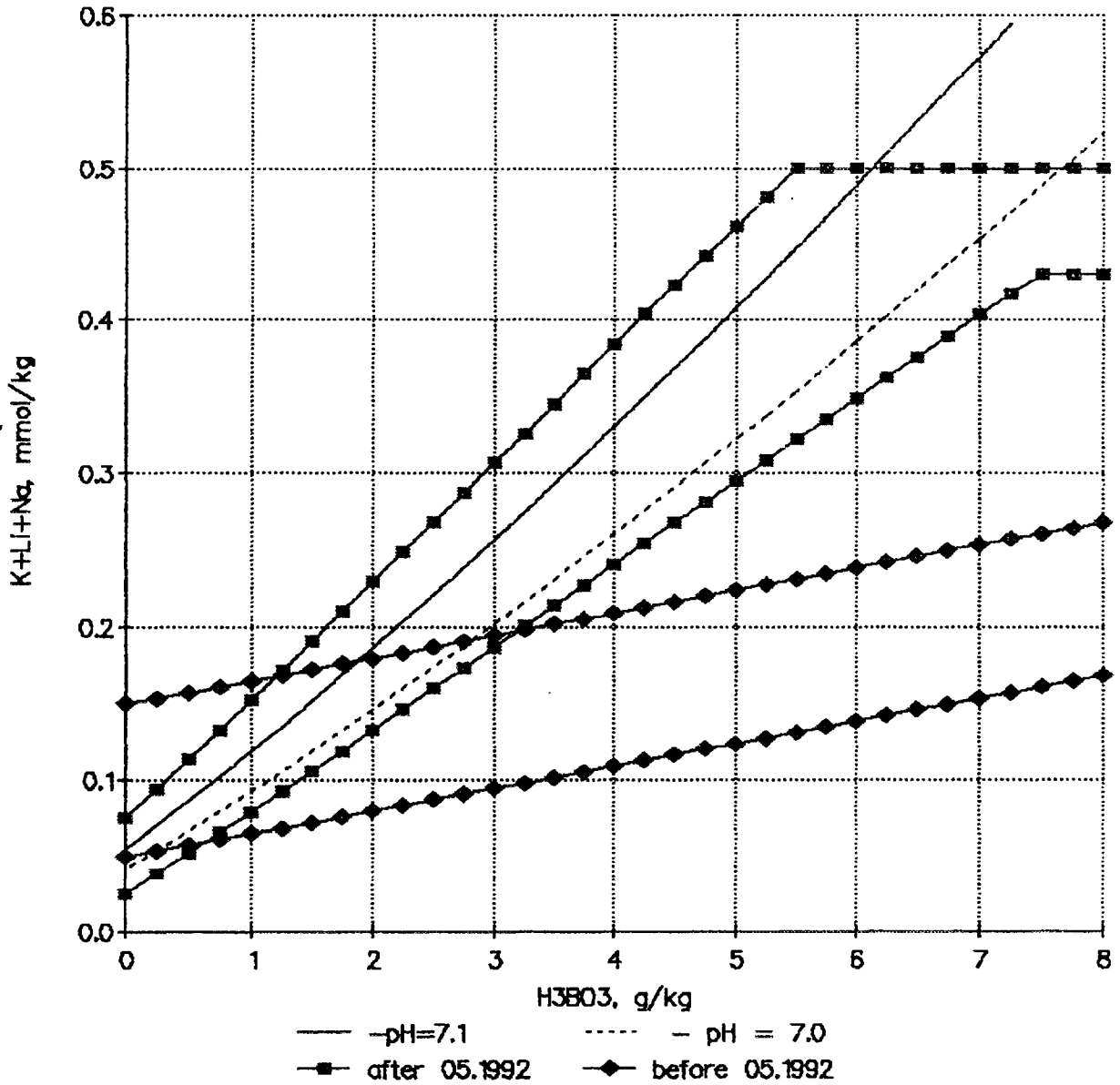


FIG. 2 WWER-1000 pH<sub>290</sub> (NH<sub>3</sub>=15 ppm)

TABLE I Mean Values and Variation Ranges in Main-Coolant Quality Characteristics in First Loop of NPP with WWER-1000 in 1990

NPP	Unit N	Quality characteristics					Proportion of time norm observed, %	
		pH	NH <sub>3</sub> ppm	H <sub>2</sub> nm1/kg	Fe ppb	Cu ppb	K+Li+Na	H <sub>2</sub>
The regulation limit		5.7-10.2	≥ 5	30-60	≤ 200	≤ 20	-	-
New-Voronezh	5	7.84+0.78 7.00-9.40	13+3 8-17	34+2 31-38	22 10-80	≤ 3	100	100
Kalinin	1	7.74+0.34 7.20-8.20	19+3 15-23	37+3 30-40	11+2 10-17	≤ 5	75	100
	2	8.09+0.75 7.30-9.60	19+2 16-22	35+2 32-38	20 10-100	5 ≤ 5-6	100	100
Balakovo	1	7.51+0.30 7.30-7.70	-	38+5 34-41	88+8 80-95	≤ 20	100	100
	2	7.99+0.59 7.10-9.20	-	37+3 32-44	69+51 20-200	19+8 7-37	83	100
	3	7.99+0.63 7.15-8.90	-	35+3 31-41	41+18 20-70	20+12 ≤ 2-50	83	100
Zaporozhe	1	-	13+2 10-15	35+2 31-38	≤ 10	-	92	100
	2	-	13+1 13+14	34	≤ 10	-	100	100
	3	-	13+2 10+16	34+2 32-38	≤ 10	-	100	100
	4	-	12+2 9-16	33+1 32-36	≤ 10	-	92	100
	5	-	14+2 11-17	33+1 31-36	≤ 10	-	100	100
South-Ukraine	1	7.69+0.62 6.80-8.70	29+7 22-40	40+2 35-43	-	-	100	100
	2	7.92+0.56 7.10-8.60	34+6 21-43	41+4 32-44	-	-	100	100
	3	7.79+0.39 7.20-8.70	29+8 17-43	43+1 41-45	-	-	100	100
Hmel'nitsk	1	7.54+0.21 7.30-7.90	17+6 9-23	32+1 31-34	≤ 30	-	100	100
Rovno	3	7.67+0.21 7.30-8.00	19+4 12-23	36+6 31-46	10 5-30	≤ 20	92	100

mean value + standard deviation  
minimum value - maximum value

TABLE II Mean Values and Variation Ranges in Main Coolant Quality Characteristics in First Loop of NPP with WWER-440 in 1990

NPP	Unit N	Quality characteristics				Proportion of time norm observed, %	
		pH	NH3 ppm	H2 nm1/kg	Fe ppb	K+Li+Na	H2
The regulation limit		5.7-10.2	≥ 5	30-60	≤ 200	-	-
Kola	1	7.76+0.68 7.10-8.87	11+2 10-14	44+3 40-52	≤ 30	100	100
	2	7.5+0.5 7.1-8.6	11+1 10-14	44+4 39-52	≤ 30	70	100
	3	7.7+0.5 7.2-9	29+2 26-33	41+5 35-49	≤ 30	100	100
	4	7.82+0.64 7.15-9.30	27+1 24-29	42+4 35-46	≤ 30	90	100
Novovoronesh	3	8.45+1.01 7.50-10.0	9+2 7-17	36+3 32-43	12+4 ≤10-20	92	100
	4	7.77+0.52 7.30-8.90	8+3 6-16	37+7 32-57	13+5 ≤10-22	70	100
Rovno	1	7.12+0.67 6.20-8.20	15+5 11-23	42+5 35-48	≤ 5	60	100
	2	7.39+0.41 6.75-7.90	18+5 12-23	32+10 5-43	28 ≤10-22	75	92

mean value + standard deviation  
 minimum value - maximum value

TABLE III Mean Values and Variation Ranges in Main Coolant Quality Characteristics in First Loop of NPP with WWER-1000 in 1991

NPP	Unit N	Quality characteristics					Proportion of time norm observed, %	
		pH	NH <sub>3</sub> ppm	H <sub>2</sub> nm1/kg	Fe ppb	Cu ppb	K+Li+Na	H <sub>2</sub>
The regulation limit		5.7-10.2	≥ 5	30-60	≤ 200	≤ 20	-	-
New-Voronezh	5	7.38+0.50 6.90-8.20	6+2 5-10	39+5 32-45	15+7 10-30	≤ 3	55	100
Kalinin	1	7.81+0.52 7.30-9.00	18+2 15-21	33+2 31-35	10	-	88	100
	2	7.87+0.82 7.28-9.30	17+2 14-19	33+2 31-35	10	-	88	100
Balakovo	1	7.74+0.82 7.10-9.70	19+2 15-21	37+2 34-40	110+90 20-200	19+3 13-20	89	100
	2	7.43+0.31 6.90-7.70	20+2 17-22	38+2 35-40	160+60 60-200	15+3 10-20	79	100
	3	7.89+0.97 7.00-9.70	20+1 18-21	35+3 32-42	120+80 20-200	16+3 13-20	89	100
Zaporozhe	1	7.25+0.22 7.00-7.30	12+1 11-13	33+2 31-36	11+3 10-20	-	90	100
	2	7.15+0.11 7.00-7.30	13+1 11-15	33+2 31-35	≤ 10	-	78	100
	3	7.15+0.10 7.00-7.30	11+2 10-13	32+1 31-34	≤ 10	-	100	100
	4	7.15+0.09 7.00-7.30	12+2 10-15	32+1 31-33	≤ 10	-	75	100
	5	7.20+0.10 7.00-7.30	13+3 9-17	32+1 30-33	≤ 10	-	100	100
South-Ukraine	1	7.43+1.07 5.80-9.20	19+7 6-22	44+2 41-47	≤ 10	-	81	100
	2	7.51+0.77 5.70-8.60	27+8 7-36	38+3 33-42	11+2 10-15	-	79	100
	3	8.29+0.89 7.20-10.2	44+11 27-56	39+4 33-49	14+7 10-30	-	86	100
Hmel'nitsk	1	7.73+0.76 6.90-9.15	17+4 10-21	33+2 32-38	20 10-80	≤ 20	90	100
Rovno	3	7.67+0.81 7.00-9.30	16+4 9-21	40+4 33-45	9+3 3-12	-	86	100

mean value + standard deviation  
minimum value - maximum value



TABLE IV Mean Values and Variation Ranges in Main Coolant Quality Characteristics in First Loop of NPP with WWER-440 in 1991

NPP	Unit N	Quality characteristics				Proportion of time norm observed, %	
		pH	NH3 ppm	H2 nm1/kg	Fe ppb	K+Li+Na	H2
The regulation limit		5.7-10.2	≥ 5	30-60	≤ 200	-	-
Kola	1	7.46+0.33 7.10-8.00	11+2 8-16	46+6 36-55	60+30 30-110	100	100
	2	7.28+0.25 6.90-7.75	14+6 9-25	44+6 37-52	40+30 5-110	70	100
	3	8.15+0.90 7.40-9.20	32+2 29-35	39+13 4-46	≤ 30	100	100
	4	7.83+0.45 7.30-8.55	33+3 29-39	40+4 35-48	≤ 30	90	100
Novovoronezh	3	7.50+0.15 7.30-7.70	8+1 7-9	40+8 34-56	35+20 ≤10-56	85	100
	4	8.10+0.90 7.20-9.80	9+2 7-12	38+9 31-53	10+1 ≤10-12	80	100
Rovno	1	8.15+0.90 7.00-9.80	28+6 20-38	39+6 32-53	12+2 10-15	83	100
	2	8.17+0.73 7.30-9.45	26+3 23-30	38+3 35-45	13+3 10-22	78	92

mean value + standard deviation  
 minimum value - maximum value

TABLE V Mean Values and Variation Ranges in Main Coolant Quality Characteristics in First Loop of NPP with WWER-1000 in 1992

NPP	Unit N	Quality characteristics					Proportion of time norm observed, %	
		pH	NH3 ppm	H2 nm1/kg	Fe ppb	Cu ppb	K+Li+Na	H2
The regulation limit		5.7-10.2	≥ 5	30-60	≤ 200	≤ 20	-	-
New-Voronezh	5	7.36+0.39 6.80-7.90	11+8 5-30	39+7 30-51	23+10 10-40	≤ 3	75	100
Kalinin	1	7.45+0.43 6.45-8.07	19+2 16-21	33+2 30-35	15+6 10-30	-	64	100
	2	8.01+0.79 7.10-9.48	18+1 17-21	33+2 30-35	13+5 10-22	-	90	100
Balakovo	1	7.92+0.47 6.95-8.60	-	38+4 32-45	165+74 15-200	18+2 15-20	58	100
	2	7.87+0.51 7.40-9.00	-	37+3 32-42	146+77 20-200	17+3 13-20	50	100
	3	8.16+0.84 7.30-9.60	-	39+3 33-45	139+91 15-200	18+3 15-20	40	100
Zaporozhe	1	-	15+2 13-17	33+1 31-34	≤ 10	-	80	100
	2	-	15+1 13-16	33+1 32-34	≤ 10	-	80	100
	3	-	13+1 12-15	33+2 31-37	≤ 10	-	88	100
	4	-	13+1 12-16	32+1 30-33	≤ 10	-	70	100
	5	-	14+1 12-15	33+1 32-34	≤ 10	-	64	100
Rovno	3	7.58+0.68 6.60-8.90	14+5 8-23	42+3 37-48	19+12 5-38	7+3 4-12	55	100
South-Ukraine	1	7.29+0.17 7.05-7.55	29+3 6-15	43+3 40-48	10+3 10-20	-	75	97
	2	7.47+0.61 6.90-8.90	27+9 14-42	40+6 33-54	≤ 10	-	100	100
	3	7.21+0.71 7.30-9.70	44+12 14-57	38+2 36-41	≤ 10	-	81	96

mean value + standard deviation  
 minimum value - maximum value

TABLE VI Mean Values and Variation Ranges in Main Coolant Quality Characteristics in First Loop of NPP with WWER-440 in 1992

NPP	Unit N	Quality characteristics				Proportion of time norm observed, %	
		pH	NH3 ppm	H2 nm1/kg	Fe ppb	K+Li+Na	H2
The regulation limit		5.7-10.2	≥ 5	30-60	≤ 200	-	-
Kola	1	8.02+0.55 7.45-8.80	13+2 11-16	42+6 34-52	≤ 30	80	100
	2	7.52+0.66 6.7-8.8	19+11 10-38	38+5 33-46	≤ 30	67	100
	3	7.72+0.34 7.3-8.3	34+13 30-38	43+5 35-52	≤ 30	91	100
	4	8.03+0.52 7.45-9.00	32+2 30-35	42+4 35-46	≤ 30	100	100
New-Voronzh	3	7.69+0.43 7.20-8.5	7+1 6-9	41+8 32-54	35 ≤10-170	70	100
	4	7.96+0.65 7.30-9.00	7+1 6-8	43+4 39-50	16+8 ≤10-31	45	100
Rovno	1	8.16+0.92 7.70-9.90	27+4 22-32	38+2 35-42	14+11 ≤10-47	64	100
	2	7.91+0.79 6.30-9.18	25+4 18-32	39+3 34-44	15+10 ≤10-45	67	100

mean value + standard deviation  
minimum value - maximum value

TABLE VII Dosage levels for staff and associate workers on Russian and Ukrainian nuclear power stations with WWER reactors at 1991/1990

NPS	Unit N	Reactor type	Startup date	Mean individual dose, cSv/year	Collective dose, cSv	standardised exposure levels, cSv/(GWt h)
Kola	1	WWER-440	08.1973	0.46/0.49	895/984	74.6/80.0
	2	WWER-440	12.1974			
	3	WWER-440	03.1981			
	4	WWER-440	11.1984			
New-Voronezh	3	WWER-440	03.1971	0.59/0.46	1809/1269	181/129
	4	WWER-440	12.1971			
	5	WWER-1000	06.1980			
Kalinin	1	WWER-1000	0.51984	0.19/0.29	402/649	34.1/51.9
	2	WWER-1000	12.1986			
Balakovo	1	WWER-1000	12.1985	0.47/0.048	127/98	8.17/7.76
	2	WWER-1000	12.1986			
	3	WWER-1000	12.1988			
Zaporozhe	1	WWER-1000	12.1984	0.14/0.08	483/281	17.8/11.3
	2	WWER-1000	10.1985			
	3	WWER-1000	12.1986			
	4	WWER-1000	12.1987			
	5	WWER-1000	08.1989			
South-Ukraine	1	WWER-1000	12.1982	0.67/0.42	1389/1272	83.2/88.3
	2	WWER-1000	12.1985			
	3	WWER-1000	12.1989			
Rovno	1	WWER-440	12.1980	0.27/0.24	538/709	47.2/55.6
	2	WWER-440	12.1981			
	3	WWER-1000	12.1986			
Khmelnitsk	1	WWER-1000	12.1987	0.31/0.43	544/489	90.9/71.0

TABLE VIII Dosage levels for staff and associate workers on Russian and Ukrainian nuclear power stations with WWER reactors at 1991 / 1990

NPS	Unit N	Reactor type	Startup date	Mean individual dose, cSv/year	Collective dose, cSv	standardised exposure levels, cSv/(GWt h)
Kola	1	WWER-440	08.1973	0.46/0.36	895/854	74.6/79.5
	2	WWER-440	12.1974			
	3	WWER-440	03.1981			
	4	WWER-440	11.1984			
New-Voronezh	3	WWER-440	03.1971	0.59/0.48	1809/1347	181/135
	4	WWER-440	12.1971			
	5	WWER-1000	06.1980			
Kalinin	1	WWER-1000	05.1984	0.19/0.16	402/344	34.1/26.7
	2	WWER-1000	12.1986			
Balakovo	1	WWER-1000	12.1985	0.047/0.075	127/189	8.17/10.1
	2	WWER-1000	12.1986			
	3	WWER-1000	12.1988			

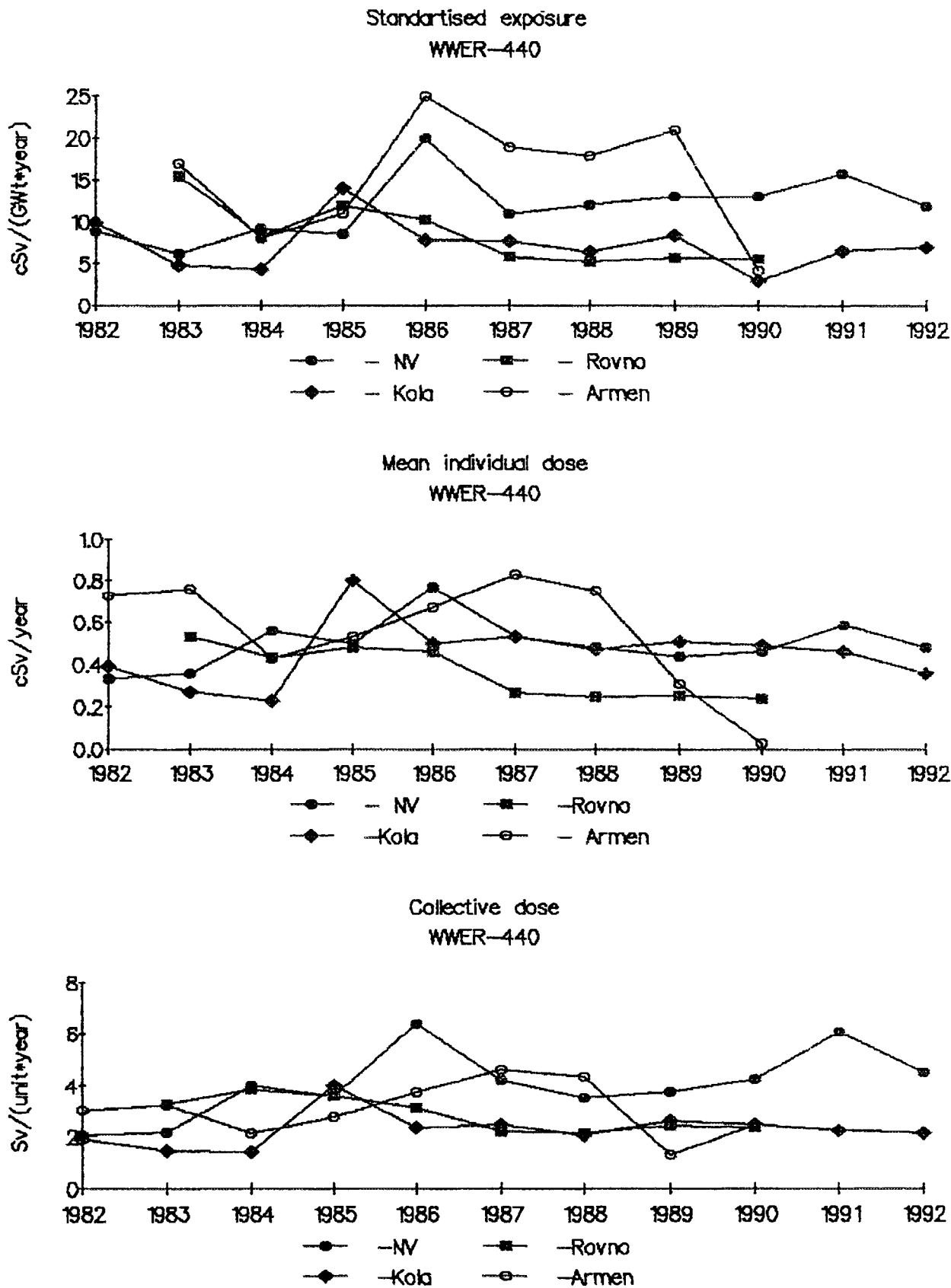


FIG. 3 Radiation exposure in Russian and Ukrainian WWER-400

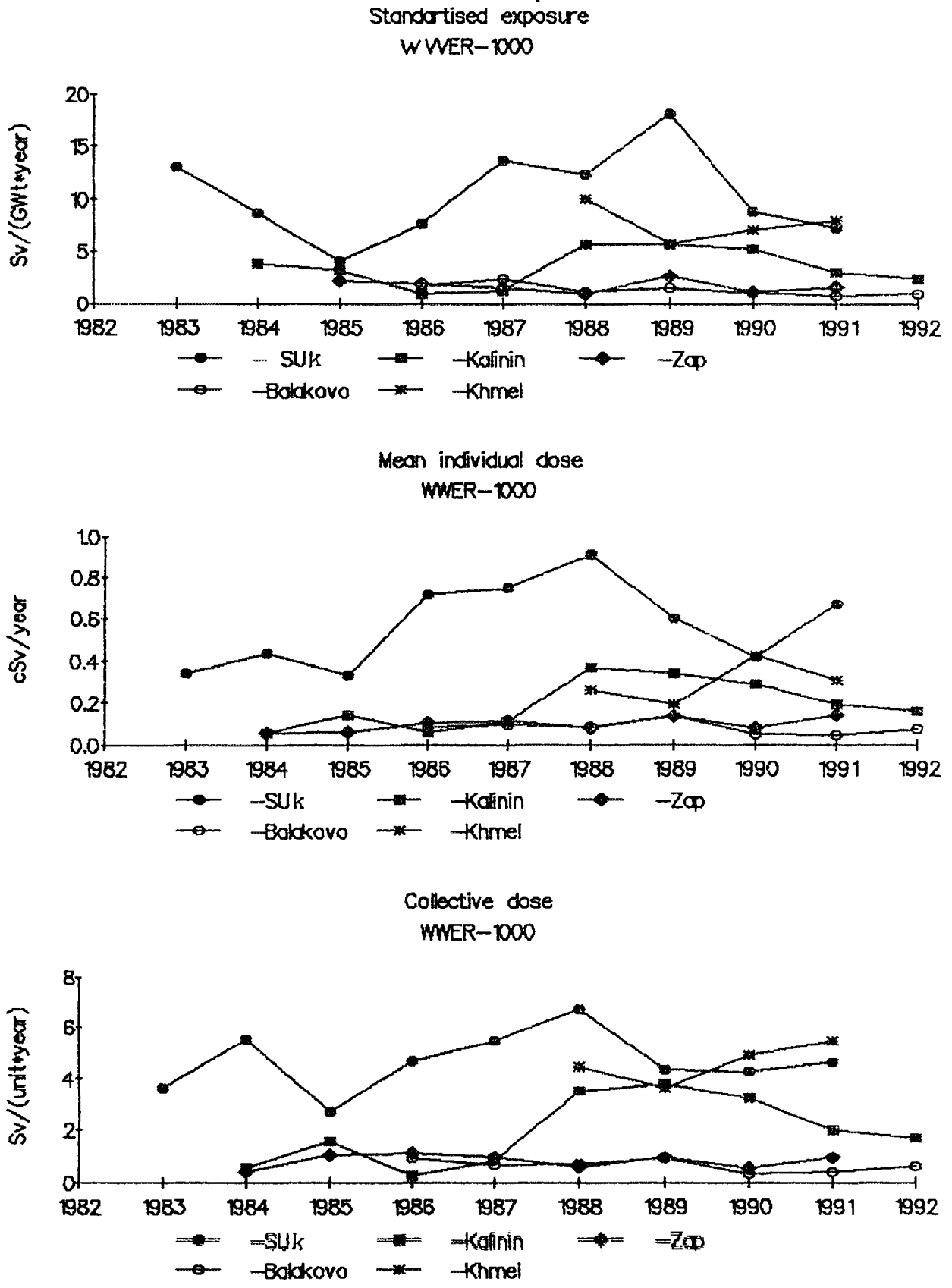


FIG. 4 Radiation exposure in Russian and Ukrainian WVER-1000

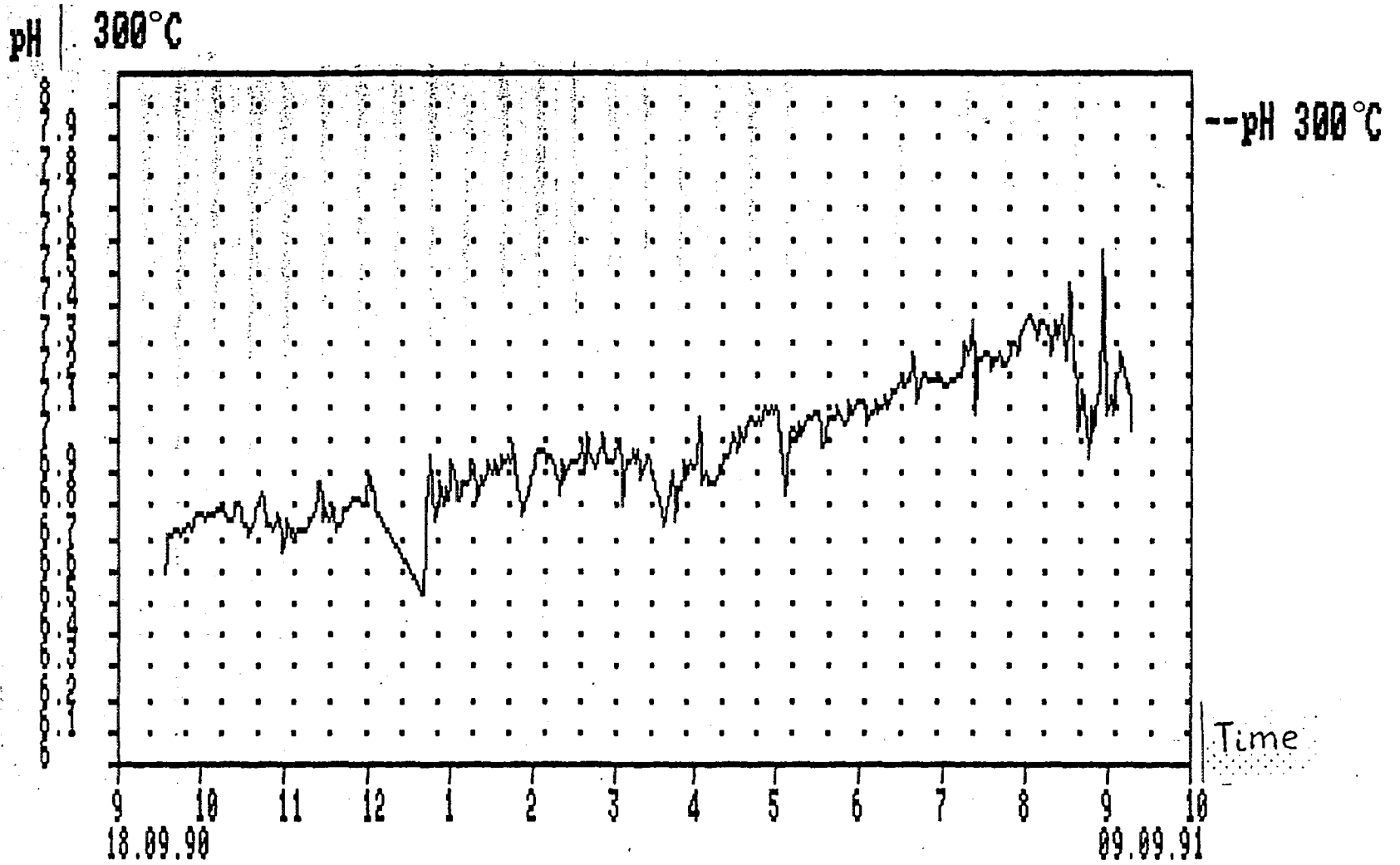


FIG. 5 Zaporozhe Unit 3 pH<sub>300</sub> during cycle 5



pH 300°C

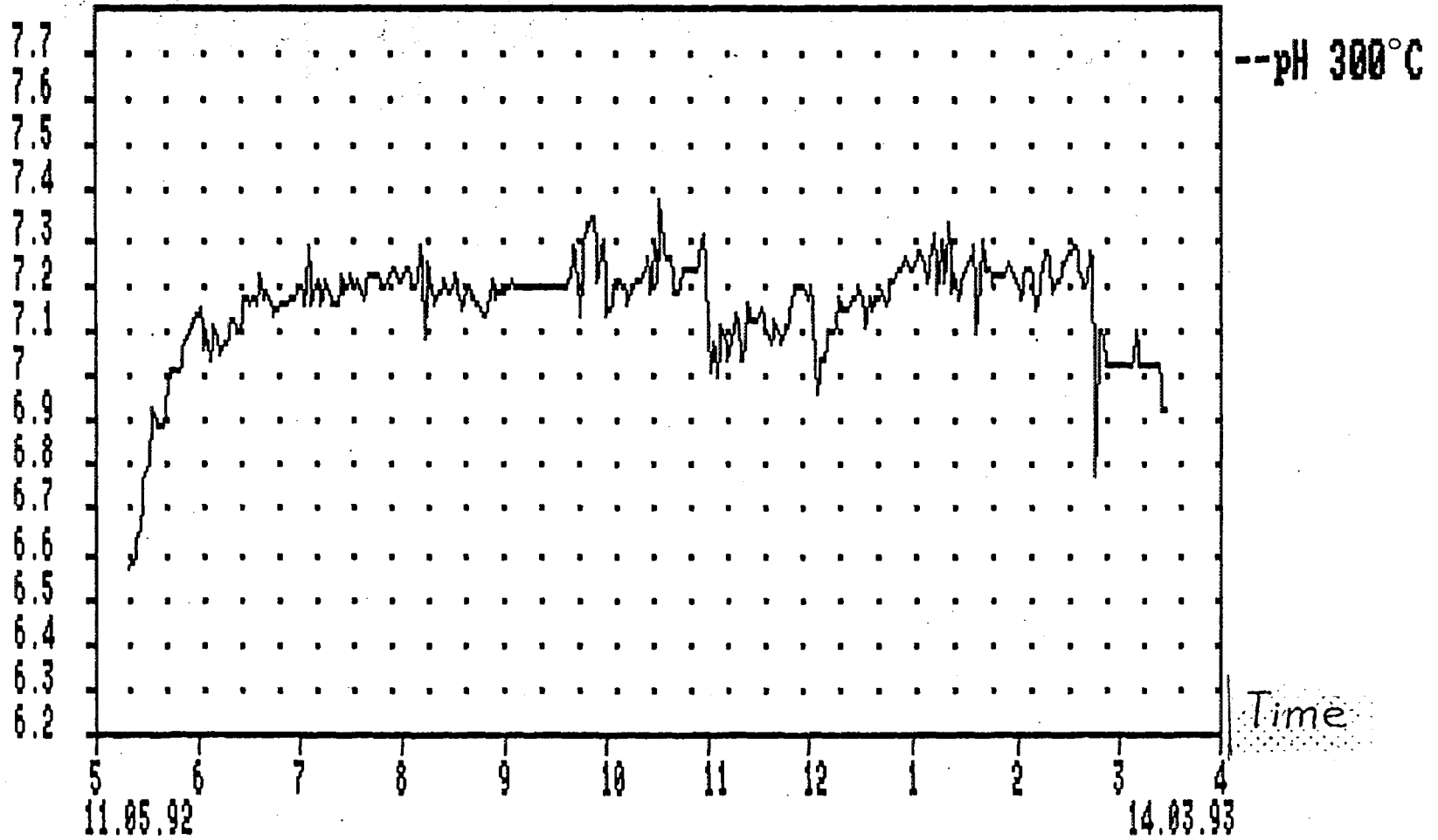
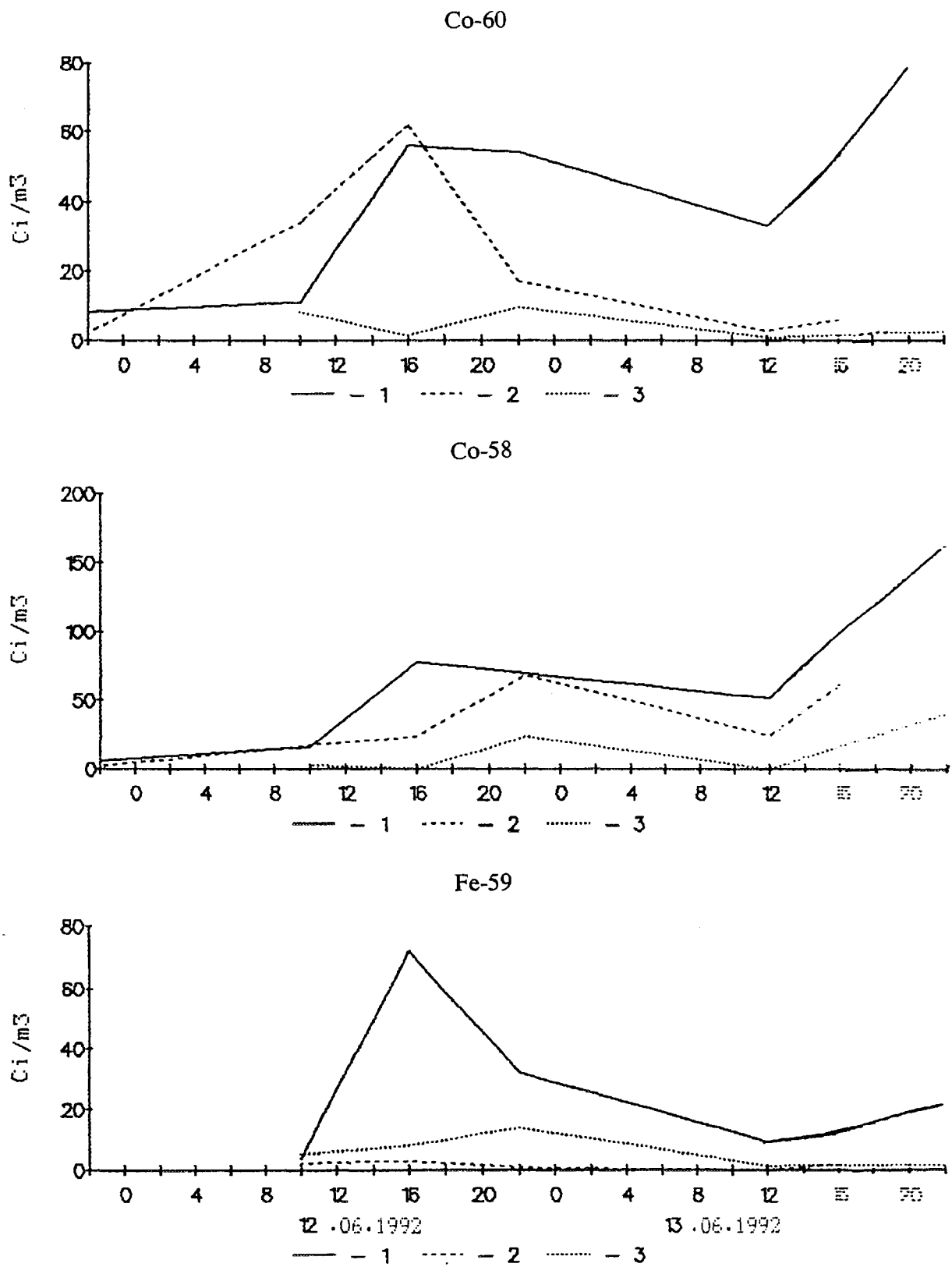


FIG. 6 Zaporozhe Unit 3 pH<sub>300</sub> during cycle 6



— 1 Primary Coolant    - - - 2 After Filter mixed bed demineralizer    ..... 3 After H<sup>+</sup> Cation Filter

FIG. 7 Variations of measured activities in primary coolant during "soft" decontamination at Kalinin NPP - 2 before refuelling (1992)

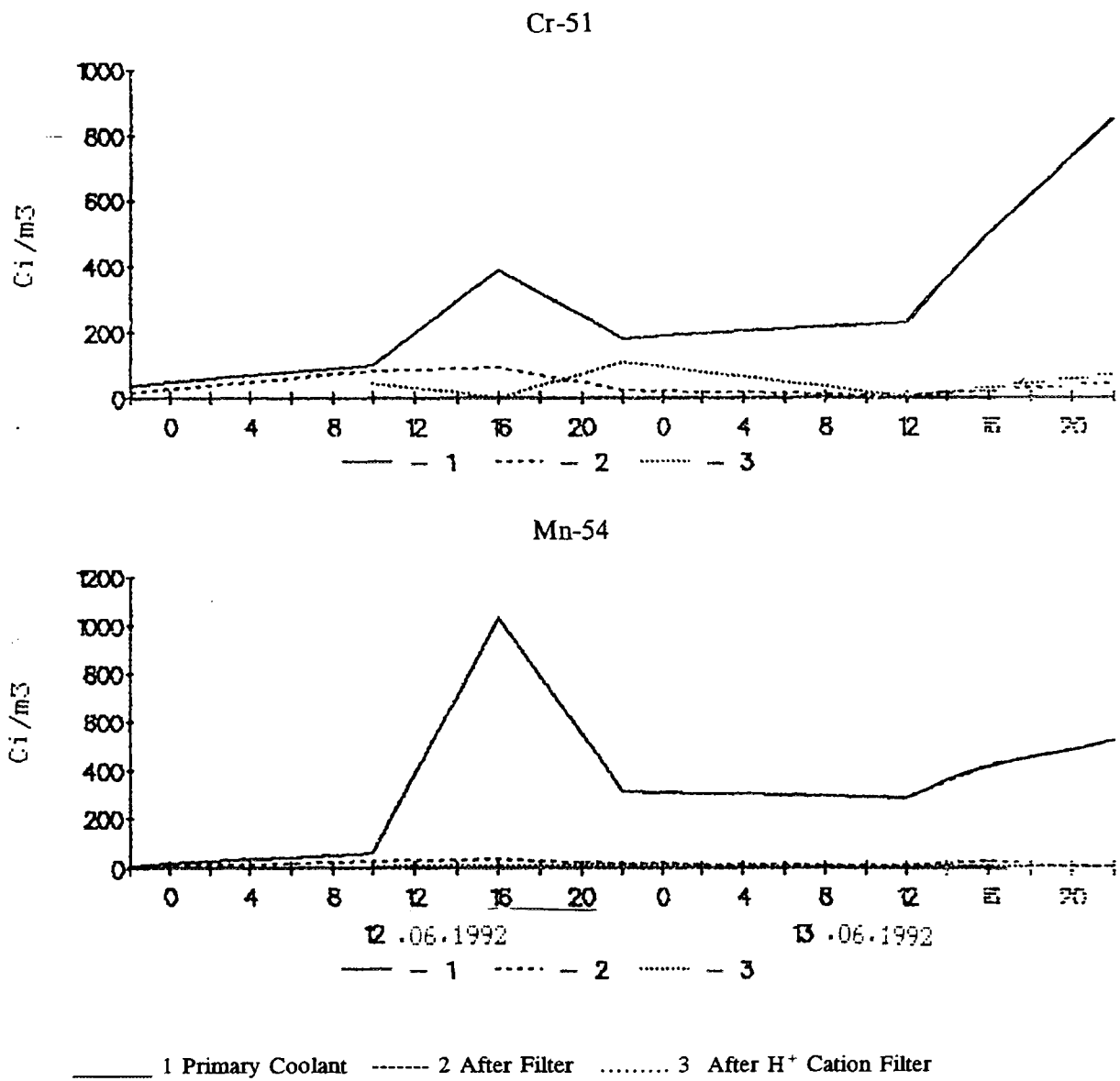


FIG. 8 Variations of measured activities in primary coolant during "soft" decontamination at Kalinin NPP - 2 before refuelling

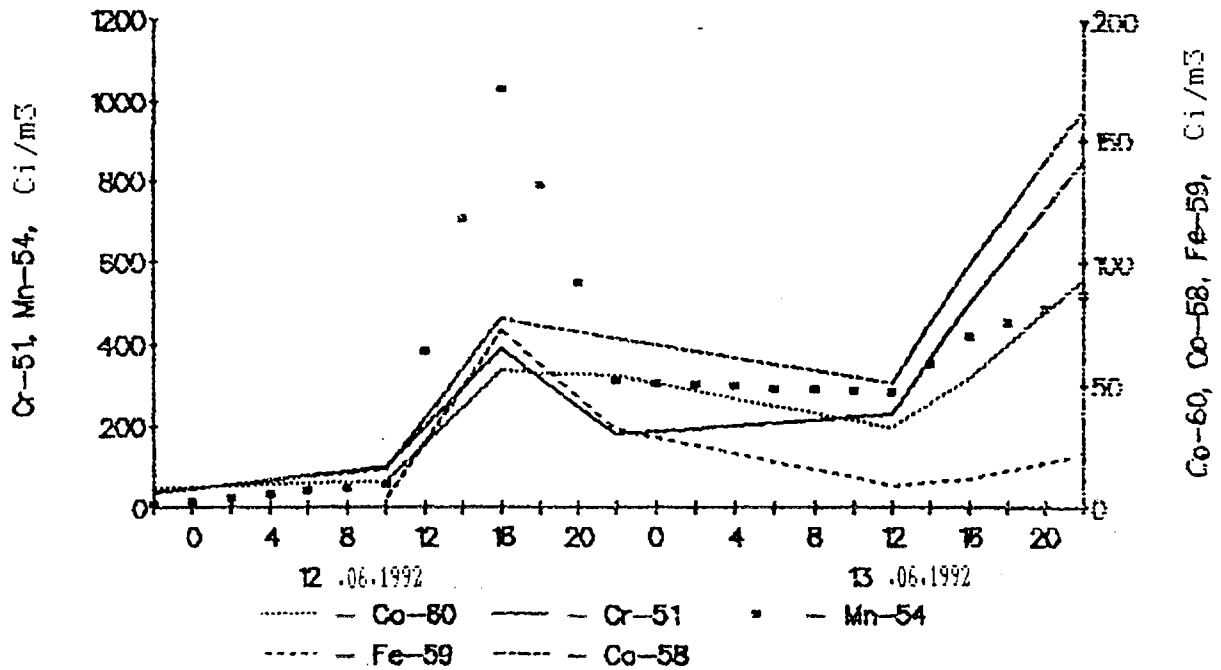


FIG. 9 Variations of measured activities in primary coolant during "soft" decontamination at Kalinin NPP - 2 before refuelling (1992)

## CONCLUSIONS

1. Russian and Ukrainian WWER operating data shows minimal collective doses and radiation fields corresponds:
  - Maximal pHt of Primary coolant
  - Maximal stability of pHt, H<sub>2</sub> and O<sub>2</sub> concentrations
2. New WWER reactors primary water chemistry guidelines (from 1992-1993) involved corrected Boron-alkali metals mode with constant pHt 7.0-7.1 at inlet reactor temperature. Optimal pHt level corresponds positive temperature gradient in zone of magnitude solubility minimum.
3. Organic impurities in primary coolant (ion exchange resins etc.) can cause carbonic deposits on fuel claddings.
4. Primary circuit soft decontamination reduce radioactive deposits on out-of-core equipment.

## SOME CONCLUSIONS ABOUT HYDRAZINE WATER CHEMISTRY

1. A hydrazine water chemistry at KOLA and ROVNO NPP accompanied by optimization and stability main coolant chemical parameters (pHt), hydrogen and oxygen concentration). As a result of both factors radiation situation improved.
2. ROVNO, ZAPOROZHE and NOVovoronezh NPP with WWER reactors use ammonia-hydrazine treatment of feed water with aim of deoxygenation. Hydrazine concentration in primary coolant is negligible.

3. KALININ, BALAKOVO and KHMELNITSK NPP use ammonia-potassium primary water chemistry. Hydrazine treatment used only at start-up with the aim of coolant degazation. At start-up hydrazine treatment of primary coolant produce protective film on stainless steel surfaces.
4. Hydrazine treatment before shut-down cause flush of accumulated corrosion products off deposits because water chemistry monitoring had to use effective reactor blow-down clean-up avoid radiation situation deterioration.
5. During operation REDOX potential of coolant at elevated temperature correlate with hydrogen concentration. The role of hydrazine addition may be connected with hydrazine capacity to accept oxydizing radicals (OH, HO<sub>2</sub>, O<sup>-</sup>) very effectively in comparison with ammonia. Ammonia-hydrazine substitution reduce oxydizing radicals production in core. It cause reduce of corrosion process and increase stability of oxide film on fuel cladding surfaces. Hydrazine radiolytic processes and chemical interaction between hydrazine and coolant impurities in real conditions must be studied.

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