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BINP'S ACCELERATORS FOR ENVIRONMENTAL APPLICATIONS

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3.1 INTRODUCTION

Electron-beam technology can be used for the solution of ecological problems relating to disinfection and elimination of toxic compounds. In 1971, the Budker Institute of Nuclear Physics (BINP) began the development and manufacturing of electron accelerators of the ELV type for application in the industrial and radiation research (Fig. 3.1). At present, the Institute offers the electron accel-

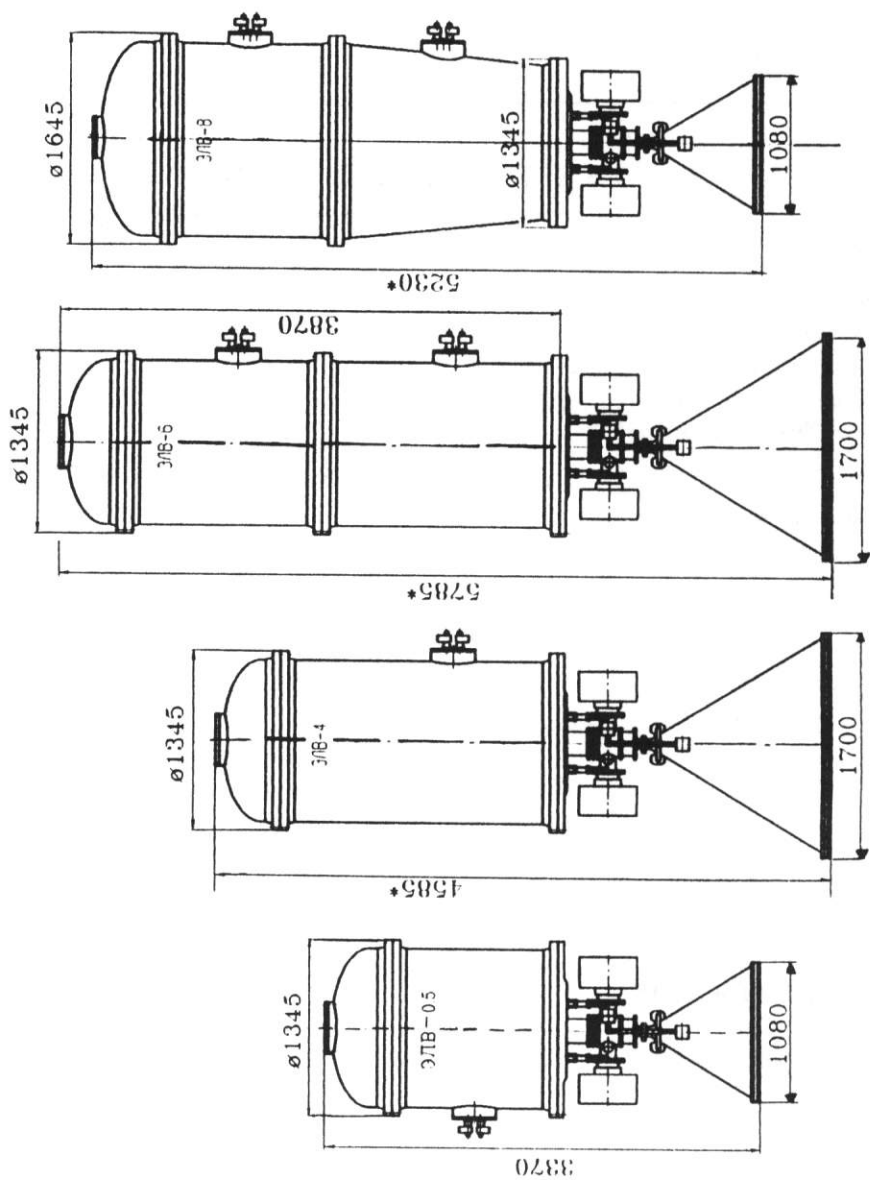


Figure 3.1 The general view of ELV-type accelerators.

erators of ELV series covering the energy range from 0.2 to 2.5 MeV with the beam current of up to 400 mA, and a maximum power of up to 400 kW. Figure 3.2 is a more detailed scheme of an ELV-4 electron accelerator. BINP has delivered over 70 accelerators of the ELV series, and their total operational time is on the order of 500 years.

The ELV-type accelerators were designed using a systems approach, thereby enabling a minimum expense for their adaptation to the specific requirements of the user by the main parameters such as the energy range, beam power of accelerated electrons, and length of extraction window, etc. The use of a gas insulation system provides the compact design of accelerator and its ease in maintenance. This systems approach also increases the accelerator reliability.

All the accelerators in this series are controlled by a similar PC (personal computer)-based system for compatibility and flexibility over a broad range of operation. The systems are fully automated and are capable of operation without an operator. The software provides all the necessary interfaces within the accelerator and between the accelerator and the process. These are monitored continuously during the operation. The program also provides a wide range of routines for the initial setting of operation modes and the accelerator adjustment.

In the majority of accelerators produced by the BINP, the electron-beam extraction is achieved through a 75-mm-wide titanium foil cooled by the airjet. Extraction devices with window length of 1 and 1.5 m are available, and, if necessary, the window length can be extended to 3 m. The operational parameter that regulates the window size is current density. The maximum linear density of a current along the window is 0.8 mA/cm with a single extraction window and 1.6 mA/cm with the double window.

The main parameters of the ELV accelerators are given in Table 3.1. Table 3.2 summarizes some of the applications that have used the ELV series electron accelerator.

More recently, an accelerator of a new design is being developed at the Institute. The range of machines will have a beam current of up to 400 mA and two accelerating tubes connected by the gas feeders with the rectifier (see Fig. 3.3). In principle, if necessary, the accelerator under development could provide the power of up to 1 MW by increasing the number of accelerator tubes.

3.2 FLUE-GAS PURIFICATION

A problem of flue-gas purification now is very real. Many methods have been studied with one of the most promising technologies involving electron-beam processing.

When the electron-beam process is used to clean the flue gas, the gas passes through an evaporative spray cooler where the gas temperature is decreased, as the humidity is increased. The gas then passes to a process vessel, where it is irradiated by a beam of high-energy electrons in the presence of a near-

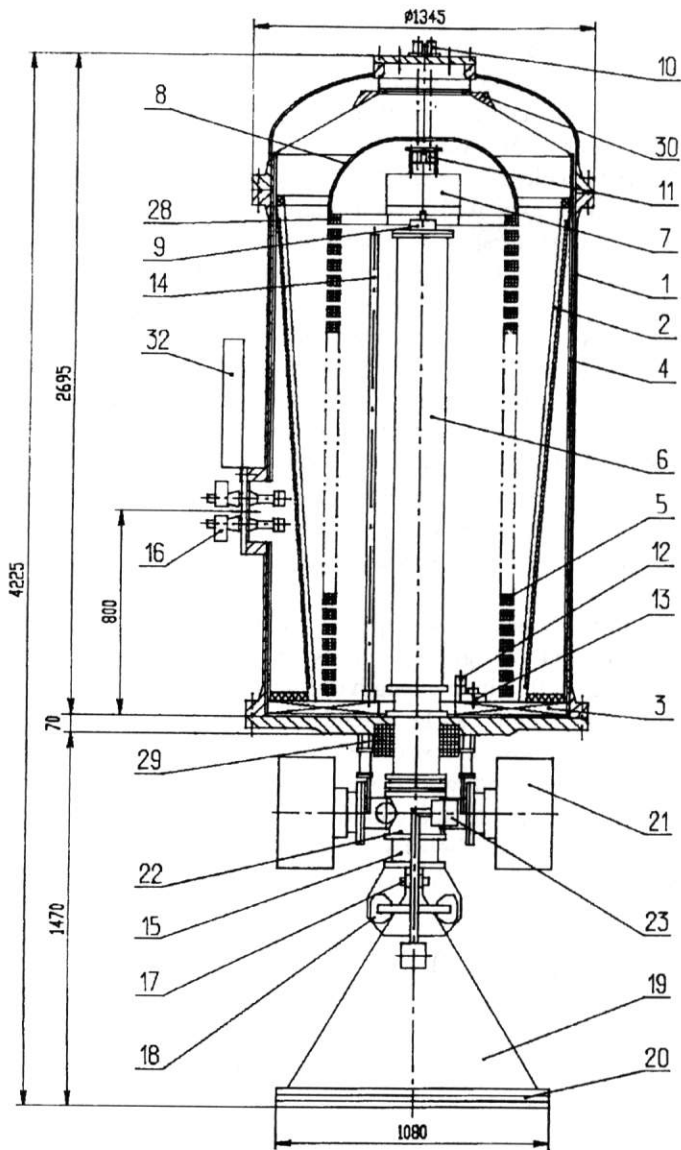


Figure 3.2 Cross section of ELV-4 electron accelerator used in the treatment system for the contaminated groundwater from the Voronezh synthetic rubber plant: 1—vessel; 2—primary winding; 3—disk magneto guide; 4—cylindrical magneto-guide; 5—rectifying section (44 pieces); 6—accelerating tube; 7—injector control unit; 8—high-voltage electrode; 9—injector; 10—“LED-PH” channel; 11—“PH-LED” channel; 12—section voltage divider; 13—capacitance unit; 14—energy divider; 15—vacuum gate; 16—primary winding terminals; 17—HF scanning coil; 18—LF-scanning coil; 19—extraction device; 20—lower frame; 21—magnetic discharge pumps.

TABLE 3.1 ELV-Type Accelerators

Accelerator Type	Energy Range, MeV	Maximum Beam Power (kW)	Maximum Beam Current (mA)
ELV-mini	0.2–0.4	20	50
ELV-0.5	0.4–0.7	25	40
ELV-1	0.4–0.8	25	40
ELV-2	0.8–1.5	20	25
ELV-3	0.5–0.7	50	100
ELV-4	1.0–1.5	50	40
ELV-6	0.8–1.2	100	100
ELV-6M	0.75–1.0	160	200
ELV-8	1.0–2.5	90	50
ELV-12	0.8–1.0	400	400

stoichiometric amount of ammonia that is injected upstream of the process vessel. Under irradiation SO_2 and NO_x containing in gas are oxidized to form H_2SO_4 and HNO_3 respectively. These acids subsequently react with the added ammonia to form ammonium sulfate and ammonium sulfate–nitrate. These salts are recovered as a dry powder using a conventional particle collector. The col-

TABLE 3.2 Environmental Applications of ELV-Type Accelerators

Place of Installation	Energy (MeV)	Power (kW)	Date of Installation	Productivity (m^3/h)
<i>Flue-Gas Treatment</i>				
Warsaw, Poland	0.5–0.7	2×50	1989	20,000
Matsudo, Japan	0.3–0.95	15	1991	1,000
Kobe, Japan	0.5	15	1994	3,000
Taejeon, Korea	0.8–1.2	40	1993	R&D
Novosibirsk, Russia	0.5–0.7	50	1991	20,000
Slavyansk, Ukraine	0.7–0.8	150	Project	100,000
<i>Wastewater Treatment</i>				
Voronezh, Russia	0.5–0.7	50	1984	120
	0.7–1.2	50	1988	
Voronezh, Russia	2.0	6×120	Project	15,000
Taejeon, Korea	0.8–1.2	40	1993	R&D
Angarsk, Russia	1.0–1.5	50	1996	800
	0.8–2.5	80	1996	1,500
Petrodvorets, Russia	2.5	2×80	Project	5,000
	2.5	2×200		
Kirishi, Russia	2.5	5×150	Project	3,300
Taegu, Korea	0.7–1.0	40	1998	50

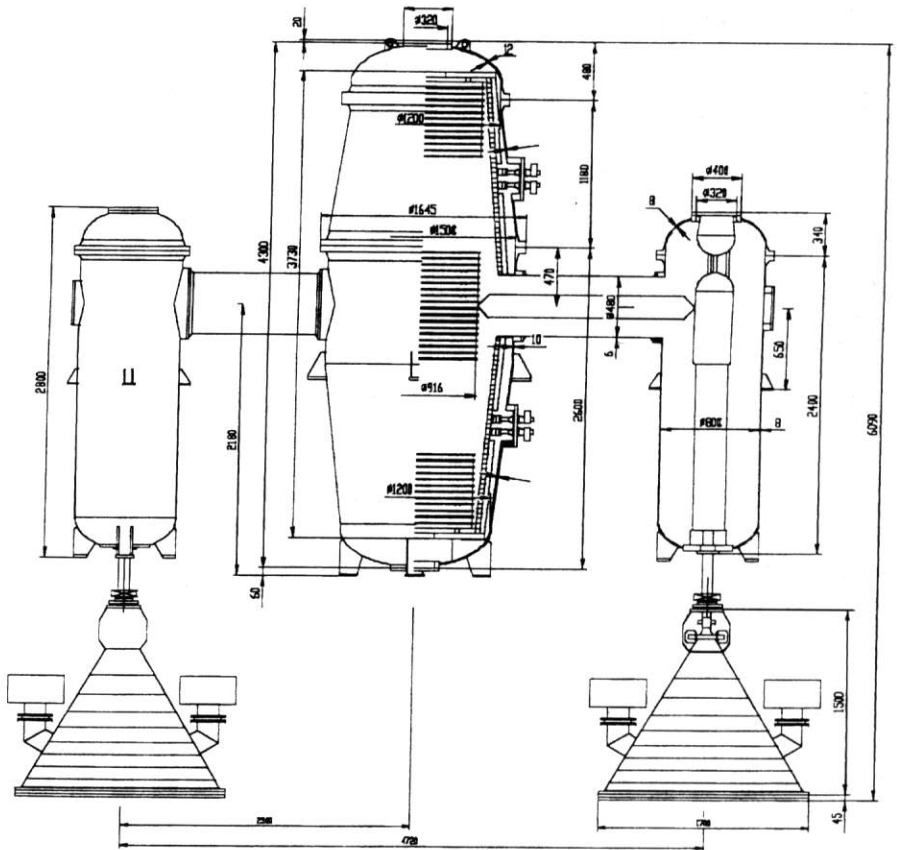


Figure 3.3 Schematic of the ELV-12 accelerator.

lected powder can be used as an agricultural fertilizer. Estimation of the required dose for the efficient SO_2 (95%) and NO_x (80%) removal shows that a 1-MW electron-beam power would be sufficient for 50–100 MW generator [1, 2].

3.3 WASTEWATER TREATMENT

Worldwide water resources have become polluted as a result of the rapid development of the chemical, plastic, pharmaceutical, and many other industries. Despite a wide range of options available for the treatment of wastewaters, there are situations where improvements could be made. These improvements may be because of the high cost of treatment or the rather narrow range of action (applicability) of each method. Electron-beam treatment of drinking water and wastewater offers another potential unit process that is ecologically acceptable. However, there are very few operating full-scale plants.

One example in Russia is a surfactant wastewater purification operation in Voronezh. The process employs two ELV accelerators, 50 kW each. The effluent volume is 5,000–35,000 m³/day. In this case the electron-beam process combined with a biological method takes place for purification of the biologically strong surface-active substance (Nekal).

The newest project in Russia now is in Angarsk city (Angarsknefteorgsintez), where two accelerators (80 and 40 kW) with maximum energy up to 2.5 and 1.5 MeV have been installed. This installation has recently been completed and is now operational. The preliminary experiments, project design, and installation were carried out by Irkutsk Research and Energofizika Development Center.

The BINP conducts cooperative investigations in the field of radiation technologies including those in environmental applications. For this purpose an ELV-6 accelerator has been installed at the Institute. Thus treatability studies of organic compounds such as ethylene glycol and phenol, polyvinyl alcohol (PVA), and dyes have been reported [3].

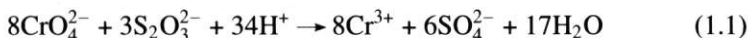
3.4 ELECTRON-BEAM TREATMENT OF SOLUTIONS CONTAINING HEAVY METALS

The use of the electron-beam process has been studied as it applies to the purification of wastewater containing heavy-metals ions. The experiments were carried out on model solutions containing following heavy metals: Cr(VI), Cu(II), Ni(II), Cd(II), Zn(II), Co(III), Pt, Pd. By varying the absorbed dose, the concentration of all these metal ions can be decreased. Some examples of electronic spectra of solutions as functions of absorbed dose are shown in Figure 3.4. Atomic absorption and inductively coupled plasma spectrometry were used for analyzing solutions before and after irradiation. Complexes of the metals with organic ligands were used for irradiation.

After a 30-Mrad irradiation, precipitation was observed in all the solutions. For complete precipitation various reducing agents were added. The results of precipitation of metals is summarized in Table 3.3. The highest efficiency was observed for Cr(VI) when Na₂S₂O₃ was the additive. In this case, the Cr(VI) concentration was achieved that met predetermined standards.

Considering the importance of such a finding, a more detailed study of solutions containing Cr(VI) was undertaken. Cr(VI) is present in tens of industrial processes such as chemical, machine industry, metallurgy, leather production, woodworking, textile, and other kinds of industry. The Cr(VI) compounds are very strong oxidants. They have adverse effects on many organisms and skin. In the contaminated soil and water, the microflora may be impaired by Cr(VI) compounds, including those used for the biological purification of wastewater.

At pH > 3, Na₂S₂O₃ is not an effective reductant:



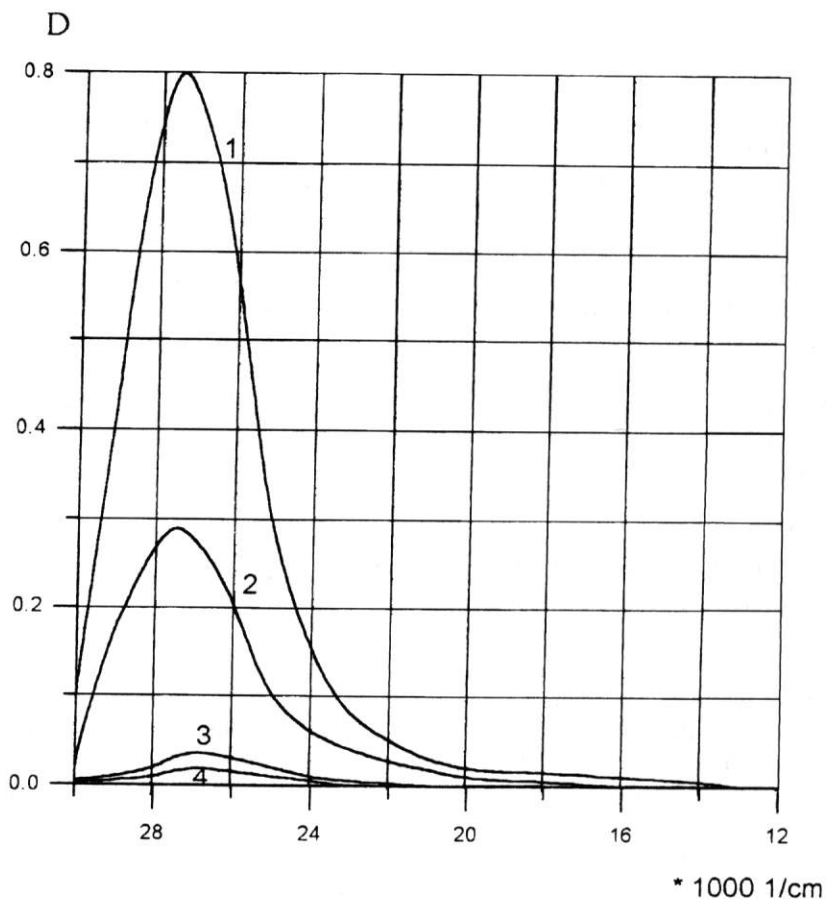


Figure 3.4 Absorption spectra of $K_2Cr_2O_7$: 1—0 Mrad; 2—1 Mrad; 3—10 Mrad; 4—30 Mrad.

Therefore, for complete removal of Cr(VI) the solution must be maintained at a low pH, and then after reduction of Cr(VI) the solution has to be neutralized ($pH \geq 7$) for precipitation of the Cr(III).

The use of irradiation with an electron beam enables the reduction reaction to occur in neutral or alkaline media with concomitant precipitation of Cr(III). Therefore multiple pH changes are not required, and there is a savings in reagents and it does not lead to generation of salts causing secondary contamination.

Our experimental results have shown high efficiency of Cr(VI) removal from model solutions when $Na_2S_2O_3$ is added to the solution. During the experiments, the concentration of the additives and pH were varied. The most interesting results are shown in Table 3.4, which shows that it is possible to achieve

TABLE 3.3 Results of Analysis of Heavy-Metal Ion Solutions

Ion	Initial Ions Metals Concentration (mg/L)	Ion Metals	
		Concentration after Irradiation (mg/L)	Additive Agent
Cr ⁶⁺ (K ₂ Cr ₂ O ₇)	2600.0	364.0	FeSO ₄
Cr ⁶⁺ (K ₂ Cr ₂ O ₇)	2600.0	168.0	(NH ₂) ₂ CS
Cr ⁶⁺ (K ₂ Cr ₂ O ₇)	104.0	2.3	Na ₂ S ₂ O ₃
Cr ⁶⁺ (K ₂ Cr ₂ O ₇)	52.01	2.5	Na ₂ S ₂ O ₃
Fe ³⁺	55.85	34.6	Na ₂ S ₂ O ₃
Co ³⁺	58.94	31.7	H ₂ O ₂
Co ³⁺	58.94	11.1	Na ₂ S ₂ O ₃
Ni ²⁺	58.71	35.7	H ₂ O ₂
Ni ²⁺	58.71	13.3	Na ₂ S ₂ O ₃
Zn ²⁺	65.38	33.7	H ₂ O ₂
Zn ²⁺	65.38	1.4	Na ₂ S ₂ O ₃
Cu ²⁺	63.34	5.9	H ₂ O ₂
Cu ²⁺	63.54	0.3	Na ₂ S ₂ O ₃

TABLE 3.4 Decreasing of Cr(VI) Concentration in Water Solutions on Electron Beam Irradiation. Reducing Agent: Na₂S₂O₃

Cr(VI) Initial Concentration, mg/dm ³	Dose, Mrad	pH	Mole S/Mole Cr Ratio	Cr(VI) Concentration After Irradiation, mg/dm ³
10	0	3	8	0.05-0.1
10	0	6.5	8	9
10	0	9	8	11
100	0	3	8	6
100	0	6.5	8	100
100	0	9	8	100
10	2	3	8	0
10	2	6.5	8	0
10	2	9	8	0.1
100	2	3	8	0
100	2	6.5	8	16, 3
100	2	9	8	0
10	10	3	4	0
10	10	6.5	4	0
10	10	9	4	0
10	10	3	8	0
10	10	6.5	8	0
10	10	9	8	0

complete precipitation of Cr(VI), which is very important. In addition to removing the Cr(VI) from solutions, another advantage is that highly concentrated metal sediments, appropriate for further use, are obtained.

Moreover the economic analysis suggests that the electron-beam method is competitive with chemical precipitation when ferrous sulfate (FeSO_4) is used [4]. Further investigation of solutions of heavy metals is required.

Similar to sodium thiosulfate, two other sulfur-containing sodium salts—sulfite (Na_2SO_3) and sulfide (Na_2S)—are good reducing agents for Cr(VI). At a certain S/Cr mole ratio in an acid medium, all three reducing agents are capable to reduce the Cr(VI) concentration to Limiting Admissible Concentration. However, it requires preliminary acidification and subsequent alkalization of the sewage. Na_2S is the most active reagent in this process, followed by Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_3$.

Under an electron-beam, Cr(VI) can be reduced with all three reagents not only in an acid medium but also in neutral or basic medium. These results are shown in the Table 3.5 and in the Table 3.6 for Na_2SO_3 and Na_2S reducing agents correspondingly. $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2S are the most active reagents, whereas Na_2SO_3 is active only at high irradiation doses. This effect is most

TABLE 3.5 Decreasing of Cr(VI) Concentration in Water Solutions on Electron Beam Irradiation. *Reducing Agent: Na_2SO_3*

Cr(VI) Initial Concentration, mg/dm^3	Dose, Mrad	pH	Mole S/Mole Cr Ratio	Cr(VI) Concentration After Irradiation, mg/dm^3
10	0	3	8	0
10	0	6.5	8	2
10	0	9	8	10
100	0	3	8	0
100	0	6.5	8	26
100	0	9	8	100
10	2	3	8	0
10	2	6.5	8	0.8
10	2	9	8	7.0
100	2	3	8	0
100	2	6.5	8	0
100	2	9	8	78.8
10	10	3	4	0
10	10	6.5	4	0.5
10	10	9	4	7
10	10	3	8	0
10	10	6.5	8	0.2
10	10	9	8	6.5

TABLE 3.6 Decreasing of Cr(VI) Concentration in Water Solutions on Electron Beam Irradiation. *Reducing Agent: Na₂S*

Cr(VI) Initial Concentration, mg/dm ³	Dose, Mrad	pH	Mole S/Mole Cr Ratio	Cr(VI) Concentration After Irradiation, mg/dm ³
10	0	3	8	0.03–0.05
10	0	6.5	8	5
10	0	9	8	12
100	0	3	8	0
100	0	6.5	8	11
100	0	9	8	100
10	2	3	8	0
10	2	6.5	8	0
10	2	9	8	0
100	2	3	8	0
100	2	6.5	8	0
100	2	9	8	0
10	10	3	4; 8	0
10	10	6.5	4; 8	0
10	10	9	4; 8	0
10	10	3	4; 8	0
10	10	6.5	4; 8	0
10	10	9	4; 8	0

likely caused by the fact that electron-beam initiates not only the water radiolysis but also chain processes with participation of sulfurous compounds. Na₂S₂O₃ and Na₂S are inclined to such reactions. The latter can form polysulfides, which easily give rise to free sulfurous radicals with subsequent chain propagation and branching reactions.

The treatment of aqueous solutions of Pt and Pd using the high-energy electron-beam process with a dose of 30 Mrad presents the possibility of separating these metals from solution. After irradiation the metals formed particles that would easily settle or, in the case of Pt, a colloidal solution.

Table 3.7 summarizes the analytic results of the irradiated solutions. These data demonstrate that an electron-beam provide precipitation of considerable amount of Pt and Pd as metallic particles.

In the case where the highly stable colloidal Pt particles (of 0.5–1.0 μm) were produced, they can be coagulated or used for industrial purposes, for example, obtaining Pt catalysts on highly developed surfaces. Thus, using the electron-beam process solutions with low concentrations of Pt and Pd may be processed and the Pt and Pd recovered and reused.

TABLE 3.7 Results of Analysis of Platinum- and Palladium-Water Solutions

Compound	Ion Metals Concentration (g/dm ³)		Sediment
	Initial	After Radiation	
H ₂ [PtCl ₄]	0.485	0.015	Metallic platinum
K ₂ [PtCl ₄]	1.0	0.01	Metallic platinum
H ₂ [PtGly ₄]*	0.45	—	Metallic platinum
K ₂ [PdCl ₄]	0.318	0.0086	Metallic palladium
[t-PdCl ₂ (NH ₃) ₂]	0.359	0.018	Metallic palladium
[Pd(MetOH)Cl ₂]**	0.0762	0.0078	Metallic palladium

*Gly-glycine

NH₂CH₂COOH

**(MetOH-metionin)

3.5 VORONEZH SYNTHETIC RUBBER PLANT

From the late 1940s until the early 1960s the Voronezh synthetic rubber plant used underground injection for its wastewater disposal. The wastewater consisted mainly of a surface-active substance. Nekal, sodium diisobutyl naphthol sulfonate. This method of disposal resulted in the contamination of the groundwater supply in an area of approximately 75 km². This area was also the site for apartment complex, and it became necessary to develop a plan for a safe source of drinking water. The plan that was developed examined two alternatives; the first was to find a treatment technology for the contaminated groundwater, and the second option was to construct a long water supply pipeline from another region of the city. The second option was dismissed as being too costly.

Several of the factors that were considered in evaluating options for the treatment of the Voronezh synthetic rubber plant contaminated groundwater were

- The volume of the contaminated groundwater (tens of millions of cubic meters) was large.
- The concentration of the pollutant was known to be up to 150–200 mg/L, and its concentration varied substantially throughout the contaminated area.
- The water to be treated foamed when aeration or ozone was applied.
- The surface-active substance (detergent), Nekal, was resistant to biological treatment.
- Nekal was poisonous to biological systems at high concentrations.

One of the most important considerations was that the concentration of Nekal, 150–200 mg/L, was 300–400 times above the maximum concentration level (MCL) for drinking water of 0.5 mg/L.

Preliminary studies showed that it was possible to employ the electron-beam

technology as part of the treatment system [5]. The advantages of this technology for treating this contaminated groundwater were

- Elimination of use of harmful chemical substances
- Compatibility with many traditional treatment processes
- Possibility of removing many pollutants
- Versatility in the treatment of various wastes (water, sewage sludge, and silt)
- High treatment rate of the process
- Efficient energy consumption
- Small industrial area
- Possibility of being fully automated
- Facility used standard electrotechnology equipment
- Absence of radioactive contamination and residual activity

Because of the volume of the contaminated water, the treatment of the water itself would have been prohibitive. However, it was possible to destroy a majority of the Nekal by treating the foam with the electron-beam process. The foam was formed by injecting a mixture of ozone/oxygen into the water. This system removed the Nekal from the water as a foam and minimized the dose necessary to destroy the contamination. Using this process design, it was possible to treat 5000–35,000 m³/day, depending on the concentration of Nekal in the groundwater. The destruction of the Nekal was facilitated by the high concentration of both ozone and oxygen in the foam, as well as the large surface area of the bubbles (Fig. 3.5).

During treatment of the water, the concentration of the Nekal decreased by approximately 75%. The concentration in the water after the “foam” treatment was 30–50 mg/L (sometimes higher), still above the acceptable level. However, as it turned out, the residual Nekal had been changed by the electron-beam treatment into the form that was easily oxidized by the biological treatment system. After biological treatment of the water, there was little or no detectable Nekal.

It should be noted that water containing Nekal prior to treatment with the electron-beam process was not compatible with the biological treatment process, whereas water containing the same apparent concentration, 50 mg/L, Nekal, was easily treated by the biological process after the electron-beam process. These results indicate that the contamination identified after the electron-beam treatment of groundwater as Nekal was probably a reaction byproduct that was biodegradable, and not Nekal. In fact, it was later established that the electron-beam treatment of the foam removed the butyl groups from the Nekal molecule.

As a result of the treatment plant and 12 years of operation, several obser-

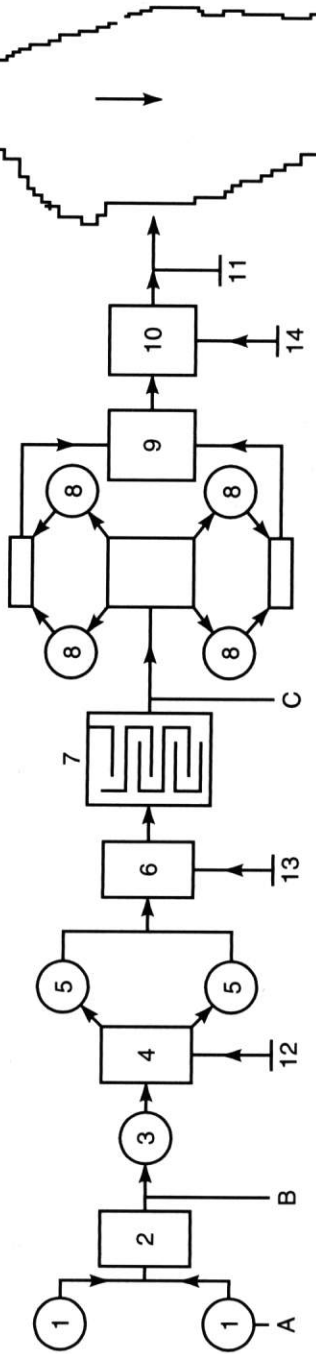


Figure 3.5 Scheme for electron-beam treatment of a contaminated groundwater from the Voronezh synthetic rubber plant (VSRP) containing the surface-active substance Nekal: 1—wells (5000–35,000 m³/day); 2—electron accelerators; 3—pump room; 4,6,10—flow equalization and mixing tanks; 5—settling tanks; 7—air tanks; 8—second settling tanks; 9—tanks; 11—pour-off of wastewater (235,000 m³/day); 12—industrial wastewater after first technological line VSRP; 13—municipal wastewater (20,000–50,000 m³/day); 14—industrial wastewater after second technological line VSRP (165,000 m³/day). Maintenance of Nekal: A—150–200 mg/L; B—40–50 mg/L; C—<0.5 mg/L.

variations are possible:

- It was possible to remove the pollutant from the water as a foam by bubbling a mixture of ozone/air through the groundwater to be treated.
- The overall required power was reduced by treating the foam.
- The ozone that was used was that generated by electron beam (window cooling flow), and therefore no additional costs were incurred to generate ozone.
- The electron-beam system was found to be compatible with a biological treatment system, thereby reducing overall treatment costs.

It was also apparent that the use of the foam process resulted in

- Pollutant concentration in the treatment system increased.
- Chain reactions were initiated increasing efficiency of the system.
- Increased surface area increased the contact with air.
- The density of the irradiated material was reduced and resulted in an increase in irradiation penetration.
- The biologically resistant Nekal was converted into a biodegradable form of the sulfonate salt.

Two accelerators 1-ELV-3 and 1-ELV-4 produced by BINP were operated on this site. The first one was placed in operation in 1984 and the second in 1988. The total power was 100 kW. These accelerators were completely automated and controlled by personal computer. Each accelerator operated an average of 7000–7500 h per year. Long-term operation of the installation showed that the process was highly efficient and had a good record of reliability. The operation of this installation provided substantial economic gain. At present the plant is shut down and the electron accelerators are being prepared for other projects. Years of operation beginning in 1984 resulted in a substantial decrease in the areal extent of the contamination, from 75 to 15 km², as shown in Figure 3.6. However for the complete cleaning of the whole site 8 years was demanded yet and only in 1996 the installation accomplished the task on purification of groundwater.

In conclusion, the development of this groundwater treatment system resulted in a plant that was easy to design; the components were all available; and the building, assembly, and extended duration of operation were no more difficult than other technological solutions. The only problem encountered was an unexpected problem associated with the formation of the foam at full scale. As it turns out, the laboratory studies were not adequate for the design of the full-scale plant, and modifications had to be engineered at the time the plant was put into operation. All the operational problems were eliminated when the second electron accelerator with an electron energy of up to 1.2 MeV was placed in operation in 1988.

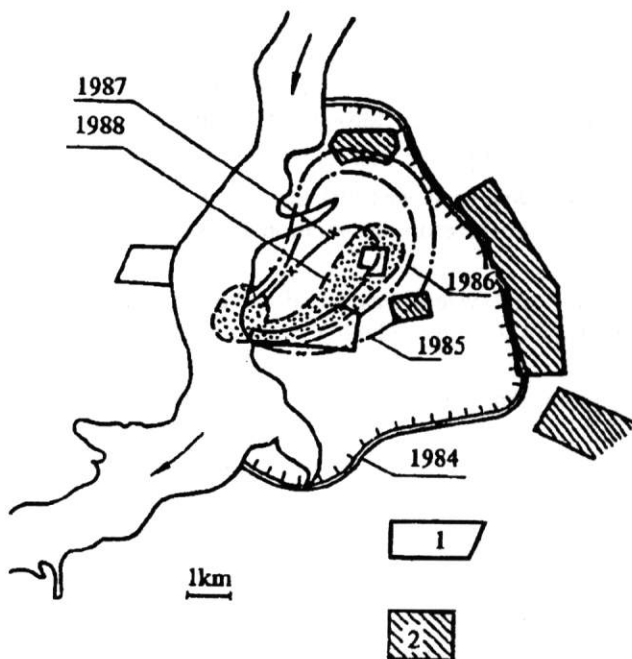


Figure 3.6 Change of contamination area during operation of the installation of electron-beam treatment of wastewater (groundwater) with biologically strong surface-active substance in region of the Voronezh synthetic rubber plant. Sources for obtaining drinking water: (1) area closed as source of drinking water before groundwater treatment system installed; (2) area opened as a source of drinking water after groundwater treatment system was operational.

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