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Periodic Table of chemical elements and Soviet atomic project[1]

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The Soviet atomic project, also known as the nuclear shield, is a true triumph of the Periodic Law. Unlike other global projects, it covers the entire Periodic Table of chemical elements: from the first element of the table (hydrogen) to the last one at the time of the project's completion (plutonium). The article, based on rare open publications, describes the main stages and chemical-technological issues surrounding the creation of atomic and thermonuclear weapons – the main goal of the nuclear shield. New fundamental results of the chemistry and technology of isotopes of hydrogen, lithium, beryllium, polonium, uranium, and plutonium have been obtained that could significantly expand the Periodic Table of chemical elements.

Keywords: *Soviet atomic project, Periodic Table of chemical elements.*

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Периодическая таблица химических элементов и советский атомный проект

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Советский атомный проект или, по-другому, ядерный щит, является подлинным триумфом Периодического закона. В отличие от других глобальных мировых проектов, он единственный охватывает всю Периодическую таблицу химических элементов: от первого элемента таблицы (водорода) до последнего на момент завершения проекта (плутония). В статье на основе редких открытых публикаций рассмотрены основные этапы и химико-технологические проблемы создания атомного и термоядерного оружия – главной цели ядерного щита. При этом получены новые фундаментальные результаты по химии и технологии изотопов водорода, лития, бериллия, полония, урана и плутония, существенно расширившие Периодическую таблицу химических элементов.

Ключевые слова: *советский атомный проект, Периодическая таблица химических элементов.*

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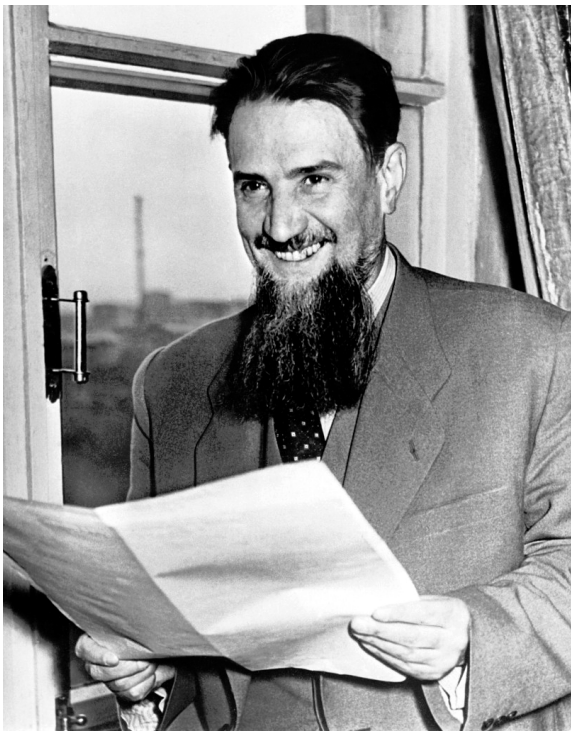
The official start date for the Soviet atomic project (SAP) was September 28, 1942. Today, September 28th is celebrated as the Day of the Nuclear Engineer in Russia. Back then the Chairman of the Council of Defense of the USSR J.V. Stalin (the actual head of state) signed a document "On the resumption of our work on the study of the possibility of obtaining explosives or energy in the fission of uranium nuclei." The basis for such a document was reliable intelligence data that Germany (the Soviet Union's enemy in World War II) and the United States, together with England (the USSR's allies), were secretly developing a new atomic weapon of unprecedented power.

The Soviet Union was shedding blood in the difficult fight against fascism and could not allocate significant resources to the new nuclear project. In addition, at a meeting between J.V. Stalin and luminaries of Soviet science (V.I. Vernadsky, A.F. Ioffe, P.L. Kapitsa, and S.I. Vavilov), the academics all expressed doubt about the creation of the bomb. All this determined the insignificant amount of resources at the project's inception. Special laboratory No. 2 was created to work on the project, headed by Igor Vasil'evich Kurchatov, on the recommendation of A.F. Ioffe. This appointment turned out to be an excellent solution. I.V. Kurchatov was a well-educated physicist-chemist, possessed extraordinary engineering intuition, and before the war he led the uranium group at the Physicotechnical Institute, headed by A.F. Ioffe, and was personally familiar with a very narrow circle of specialists in radiochemistry, chemical physics, and atomic nucleus physics.



Igor Vasil'evich Kurchatov

After the atomic bomb explosions over the Japanese cities of Hiroshima and Nagasaki in August 1945, it became clear that the United States possessed a monopoly on atomic weapons. The response of the Soviet government was instant. On August 20, 1945, the First Main Directorate for the industrial implementation of SAP was created under the USSR Council of Ministers, headed by Minister of Ammunition B.L. Vannikov, and the scientific supervisor was I.V. Kurchatov. The Minister of the Interior, Lavrentiy Pavlovich Beria, was appointed the head of SAP by the Politburo. From this moment, work on the creation of the "Nuclear shield" began developing at a tremendous speed with the involvement of all obtainable resources. And after four years, on August 29, 1949, the first Soviet atomic bomb was detonated. Later on August 12, 1953, a Soviet thermonuclear bomb was detonated. The USA's monopoly on nuclear weapons was eliminated.

The creation of nuclear weapons required tremendous effort from chemists and technologists. New knowledge was gained about the isotopes of many elements and the technologies for their production were developed. New sections appeared in chemical science: radiochemistry, radiation chemistry, nuclear chemistry, and radionuclide control. New subtle chemical technologies for radioactive elements were developed. Many thousands of chemists and technologists worked on the tasks of creating atomic and thermonuclear explosives. And all this took place in an atmosphere of strict secrecy. Very often, even colleagues from one laboratory did not know about the work of their neighbors. Nuclear industry veterans understood this completely: not a single secret flowed from SAP enterprises, and in many areas of chemical technology the Soviet Union was able to significantly overtake its rivals.

And only 50 years after the start of SAP, the leadership of the country and the Ministry of Atomic Energy and Industry of the USSR decided to partially declassify the Soviet Union's achievements in the scientific and technological issues surrounding the creation of the nuclear shield [1–3]. Over that half-century, many active participants in SAP have passed away, and information about their work and achievements must be found in the memoirs of former young employees of institutes and factories, and in separate brochures issued in small print runs (300–500 copies).

A typical example of the loss of detailed information about work in SAP is the situation regarding the remarkable rector of the M.V. Lomonosov Moscow Institute of Fine Chemical Technology, Kirill Andreevich Bolshakov (1906–1992). From the encyclopedia and Wikipedia you can find out that K.A. Bolshakov was a Soviet inorganic chemist, one of the founders of the industry of rare elements in the

USSR. It is also reported that from 1933 to 1971, he worked at the M.V. Lomonosov Moscow Institute of Fine Chemical Technology, having gone from assistant to rector. He was also awarded two Orders of Lenin, received two Stalin Prizes and a high scientific rank as a corresponding member of the Academy of Sciences of the USSR. But the details about his achievements are only in the brochure "The First Lady of Soviet Atomic Science. Collection of articles dedicated to the 100th birthday of Z.V. Ershova" [4].

It turns out that from 1930 to 1947 K.A. Bolshakov was also head of the laboratory at the State Institute of Rare Metals (*Giredmet*), and from 1947 to 1953 – the head of the department in the legendary *NII-9* (now

Kirill Andreevich Bolshakov

the Academician A.A. Bochvar All-Russian Research Institute of Inorganic Materials). At *Giredmet*, he worked with Zinaida Vasil'evna Ershova to obtain metallic uranium, and then directed solving the problem of producing tritium (the heavy ^{3}H hydrogen isotope) for the first Soviet hydrogen bomb. And then never and nowhere did K.A. Bolshakov mention his participation in this work: he swore to keep these secrets for 60 years.

As his beloved student and employee Lyudmila Dmitrievna Yurchenko (dean of the faculty T, who was known at all enterprises and institutes in the uranium industry) recalled a direct question: "Kirill Andre'evich! Did you participate in the creation of the atomic bomb?" He answered: "Well what do you think, Lyusenka? Everyone participated. And two groups took away the radioactive elements technology from us. Then they sent them to Mendeleevka ...," masterfully avoiding answering the question.

Just this one example shows how much invaluable information about the outstanding Soviet developments in chemistry and technology when creating the nuclear shield did not reach the 150th anniversary of the Periodic Table of Chemical Elements (PTCE). The author of the article has worked in the uranium industry for 56 years, the past 20 of which has been enthusiastically spent in the search for materials, memoirs, and articles about the Soviet Union's remarkable scientific and industrial work in the field of problems with raw materials for SAP. Below, in the main section, we take into consideration some of these developments, which have expanded knowledge about the chemistry and technology of rare PTCE elements.

Atomic Bomb. Uranium, Graphite, Plutonium, Polonium

The atomic bomb (at the first stage plutonium, and then uranium) was created by the Germans, the Americans, and Soviet developers based on the use of fission energy of heavy element nuclei. The main contender, even before the start of the war, for the role of fissile material was the uranium-235 – ^{235}U isotope. However, natural uranium contains only 0.7% of the ^{235}U isotope. The remaining 99.3% is uranium-238. Uranium-238 was not suitable for use as an atomic charge explosive. The absence of a sufficient amount of natural uranium during SAP's initial stage, the inability to quickly create technology and equipment for enriching natural uranium from the ^{235}U isotope and intelligence data on the efforts of Germans and Americans to develop a technology for producing element number 94 – plutonium-239 led I.V. Kurchatov to the decision to create a plutonium bomb at the first stage. But uranium was also needed to obtain plutonium.

The uranium problem was the most urgent and a very difficult one for SAP. By the beginning of work in 1945, the Soviet Union had only 13.1 tons of uranium ore in the form of dumps for the production of radium-226 in the town of Taboshar, Tajik SSR. No uranium in the USSR was mined or searched for before the start of SAP. First, one had to find the areas of its origin, build mines, and plants for processing ores. The first uranium for the experimental reactor and then the industrial ^{239}Pu production reactor was obtained as a trophy in Germany, which had concentrated uranium salts obtained in the Czech Republic and Belgium (from the Belgian Congo). And only then, thanks to the efforts of Soviet geologists, miners, builders, and chemical technologists, the uranium industry was created, in which at 14 plants up to 25000 tons of natural uranium of nuclear purity were produced up until the 1970s [5–11]. These grandiose successes are rightly connected with the name of the Minister of Secondary Engineering Efim Pavlovich Slavsky [12], three-time Hero of Socialist Labor and ten-time recipient of the Order of Lenin.

Slavsky came to SAP from the post of Deputy Minister of Non-Ferrous Metallurgy. He was awarded

three Orders of Lenin for providing the Soviet Union with ultra-deficient aluminum and alloys based on it during the war. In September 1945, L.P. Beria introduced E.P. Slavsky to I.V. Kurchatov, who asked to make a batch of ultrapure graphite used as a thermal neutron moderator for an experimental reactor to produce plutonium from natural uranium. Today, it has become known that Germany significantly overtook the United States in solving the tasks of its nuclear project, but was not able to create a bomb because of an incident called the "Pote – Heisenberg error." Heisenberg, Hitler's favorite who led the atomic project, chose a neutron moderator from two

Efim Pavlovich Slavsky

options: carbon in the form of graphite or heavy water. On his instructions, the physicist-chemist Pote checked the possibilities of using graphite, but underestimated the importance of cleaning it from boron. Heisenberg made a mistake in measuring neutron drag. As a result, the use of graphite was rejected, and the Germans were unable to wait for heavy water since all the convoys had been sunk by the British.

At the same time, it was known from intelligence that the Americans had a plutonium reactor filled with graphite, but the technology for its purification was unknown. However, E.P. Slavsky and his colleagues quickly dealt with the problem of producing the required quality graphite. I.V. Kurchatov saw in him not only a well-educated chemist-technologist and metallurgist, but also a brilliant organizer. At his behest, E.P. Slavsky was ordered by Stalin to be transferred to the atomic project.

At first, the extraction and purification of uranium from impurities was carried out at Plant No. 6 (near the city of Leninabad in the Tajik SSR) using the technology developed by Marie Curie at the beginning of the century [6]. Both the quality and the extraction of uranium from the ore were unsatisfactory. Large resources were spent on numerous uranium purification operations. Due to the urgency of the problem of obtaining natural uranium from ore materials, where its mass fraction is only 0.05 – 0.14%, at the initiative of E.P. Slavsky and by order of Stalin on April 19, 1951, a special research institute of chemical technology *NII-10*, now the All-Russian Scientific Research Institute of Chemical Technology was created. During the course of SAP, graduates were recruited into it from the following leading universities: M.V. Lomonosov Moscow Institute of Fine Chemical Technology (more than five hundred people), D.I. Mendeleev Moscow Institute of Chemical Technology (almost seven hundred people), Leningrad Institute of Technology, Faculty of Chemistry, M.V. Lomonosov Moscow State University, and others. A large young team from the All-Russian Scientific Research Institute of Chemical Technology created hundreds of new technologies to produce natural uranium of nuclear purity and many other rare metals. These are mainly ion-exchange sorption and extraction technologies, the introduction of which required new solutions in organic chemistry for the synthesis of ion-exchange reagents. Thanks to this work, the All-Russian Scientific Research Institute of Chemical Technology gained worldwide fame as a "uranium institute" and as a "sorption institute." The scientific supervisor of these studies, Boris Nikolaevich Laskorin, received a high scientific rank, full membership in the USSR Academy of Sciences.

Boris Nikolaevich Laskorin

To produce plutonium, in addition to nuclear purity graphite, metallic uranium was needed. The technology for its production on the basis of the magnesium thermal method had already been developed in 1945 by Zinaida Vasil'evna Ershova [4], who worked as the head of the *Giredmet* laboratory. By the way, Z.V. Ershova defended a top secret dissertation under the direction of K.A. Bolshakov at the Moscow Institute of

Zinaida Vasil'evna Ershova

Vitaly Grigor'evich Khlopin

Fine Chemical Technology in December 1943 on the topic of determining the ^{235}U / ^{238}U ratio in natural uranium. Z.V. Ershova received the experimental data during an internship in Paris at the laboratory of Irene Curie. I.V. Kurchatov and his colleagues respectfully called Z.V. Ershova the "Russian Madame Curie." Among Z.V. Ershova's important scientific achievements at the start of the nuclear project, is the creation of a technology for the separation of polonium-210 from irradiated bismuth-209. Polonium-210, a powerful source of alpha particles placed in a beryllium sleeve, was used as a starting neutron source in the "lighter" of the first atomic bombs. The neutron generation in a polonium-beryllium source is described by the equation:

$$^{9}_{4}\mathrm{Be} + \alpha \rightarrow ^{12}_{6}\mathrm{C} + \mathrm{n}\,.$$

The formation of polonium-210 in irradiated bismuth-209 is described by the equation:

$$^{209}\mathrm{Bi} + \mathrm{n} \rightarrow ^{210}\mathrm{Bi} \rightarrow \beta \rightarrow ^{210}\mathrm{Po}\,.$$

Very little polonium is formed in the samples of irradiated bismuth, and its separation is carried out on the basis of fine chemical technologies. Incidentally, polonium heat sources were used on the Soviet Moonwalker 1 and 2 in 1975, after SAP's completion.

The permanent mentor and her kind genius was Academician Vitaly Grigor'evich Khlopin, Director of the Radium Institute in Leningrad and Chief Radiochemist of SAP.

To produce plutonium-239 during SAP, a number of industrial uranium-graphite reactors and radiochemical plants were built to treat plutonium, uranium, and fission products from irradiated uranium. The formation of plutonium-239 upon neutron irradiation of uranium-238 in a nuclear reactor is described by the equation:

$$^{238}_{92}\mathrm{U} + ^{1}_{0}\mathrm{n} \rightarrow \gamma \rightarrow ^{239}_{92}\mathrm{U} \rightarrow \underset{23.5\mathrm{min}}{\beta^-} \rightarrow ^{239}_{93}\mathrm{Np} \rightarrow \underset{2.3565\mathrm{min}}{\beta^-} \rightarrow ^{239}_{94}\mathrm{Pu}$$

Methods for producing plutonium from irradiated uranium-238 have been developed since 1946 in the first radiochemical laboratory of *NII-9*, the head of which was Z.V. Ershova. In the bowels of this laboratory, the U-5 semi-industrial facility was created, which played a significant role in developing the technology to produce plutonium preparations at the plant Mayak. From the beginning of 1947, uranium blocks irradiated in the first experimental reactor F-1 of the Institute of Atomic Energy began to arrive at U-5. Late at night on December 18, 1947, Z.V. Ershova, together with *NII-9's* young radiochemists, first received weighted amounts of the plutonium preparation (73 micrograms). This work was the first to lead to the creation of a nuclear charge from plutonium.

The epoch of the creation of the first industrial reactor and radiochemical plant for the separation and purification of plutonium-239 at the Mayak or *Chelyabinsk-40* plant is described in detail in a book by Arkady Konstantinovich Kruglov [2], who was directly involved in the construction and commission of the enterprise. The complexity of the problem of plutonium production lies in the fact that in irradiated metallic uranium for a campaign of 2–3 weeks with a mass of loaded uranium of 100 tons, only 600–700 grams of plutonium-239 is formed. This is an extremely small amount. Further processing using PUREX technology (supervisor Academician V.G. Khlopin) makes it possible to isolate plutonium, uranium and send the nitric acid solution with a huge amount of highly active radionuclides, fission products of uranium-235, for long-term technological storage. These highly active liquid radioactive wastes

(HLRW) contain long-lived cesium-137 and strontium-90, which will remain highly active for thousands of years. The accumulation of large volumes of HLRW, the handling of which is still an unresolved problem, is the main drawback of SAP's plutonium choice.

The short interval of irradiation of uranium metal blocks (2–3 weeks) is caused by the fear of a large accumulation of plutonium-241, which after a short time of beta decay turns into americium-241 – a very highly active gamma emitter. The accumulation of americium-241 in plutonium charges is an unmasking factor, complicates the handling of charges, and requires constant resources for the fabrication of products. And this is the second significant drawback of plutonium bombs.

From what has been said, it is obvious that, along with intensive continuous production of plutonium charges, an urgent and very difficult task was developed to develop technologies and equipment for isotope enrichment of natural uranium in order to increase the content of the ^{235}U isotope from 0.72 to 90%. The first stage in solving this problem is the conversion of natural uranium from solid to gaseous. It is implemented in sublimation plants by the fluorination process to obtain uranium hexafluoride UF_6. At temperatures above 64.1 °C, this compound turns into gas [14].

As in the United States, of the four known methods for isotope separation, gas diffusion was preferred [14, 15]. In 1946, Academician Isaak Konstantinovich Kikoin was appointed the scientific leader of the project and the construction of a gas diffusion plant. The main idea behind the method is that a porous septum with countless holes with a diameter of less than 0.01 μm is installed in the path of the UF_6 gas flow. Uranium-235 hexafluoride is slightly lighter than uranium-238 hexafluoride, and lighter molecules should pass through the porous septum more easily. Therefore, the gas will be enriched in a light isotope on the other side of the septum. The main difficulties of the gas diffusion method were associated with the development of porous baffles and compressor pumps for gas movement. Acres of partitions and thousands of pumps were required. The development of porous partitions and diffusion machines was carried out by many organizations with the maximum usage of all the USSR's resources. The rush to prepare for the creation of enriched ^{235}U technology was mainly due to the fact that in 1946 the United States continued to improve nuclear weapons. In the same year, two atomic bombs were detonated on Bikini Atoll in the Pacific Ocean.

By 1950, a uranium enrichment plant was built in the middle of the Urals and was able to produce several dozen kilograms of uranium ^{235}U that had 90% enrichment. About 15000 diffusion machines worked at the plant, and the consumed electric power was 250 MW. From 1949 to 1964, another three diffusion plants in Siberia were built and commissioned. The use of enriched uranium removed the environmental problems of using plutonium for charges and opened up the possibility of using atomic energy for electric generation (with 3–5% enrichment), as well as for shipboard installations on submarines (with 40% enrichment) and icebreaking nuclear fleet (with 20% enrichment).

Centrifuge technology for enriched uranium was simultaneously developed along with the gas diffusion method. The principle of operating a gas centrifuge for the separation of uranium isotopes is that in a cylindrical rotor of a centrifuge filled with UF_6, at peripheral speeds of more than 400 m/s in vacuum, heavier molecules are concentrated at the rotor wall and are lowered down. In the machine, a special role is given to the magnetic suspension, which ensures that at high speeds of rotation of the rotor, the load is removed from the support needle. The centrifuge's fast-rotating rotor is capable of efficiently separating gas molecules into light and heavy parts. The main advantage of the centrifuge method compared to the diffusion method is its low energy consumption, which decreases quite a lot, and significantly larger thermodynamic efficiency.

The transition of the factories to centrifuge technology, carried out from 1966–1972, allowed the Soviet Union to increase the separation capacity of enterprises by 2.4 times and reduce the total electricity consumption by 8.2 times. At the same time, the Soviet Union managed to conceal the existence of the developed, most progressive and economical industrial method for 30 years. Now at the Ural Electrochemical Plant [16], one and a half million centrifuges are operating, the resource of which has reached 35 years of uninterrupted service; their rotor speed is 1500 rp/s. Russia supports 40% of the world's enriched uranium production [22].

Thermonuclear (Hydrogen) Bomb. Tritium, Deuterium, Lithium

A thermonuclear bomb uses the energy of helium **He** synthesis based on the reaction of the combination of hydrogen isotopes deuterium **^{2}H** (**D**) and tritium **^{3}H** (**T**).

$$ {}^{3}_{1}H + {}^{2}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n + E_2, \quad \text{where } E_2 = \underset{\text{synthesis}}{3.5} + \underset{\text{neutron}}{14.1} = 17.6 \text{ MeV}. \qquad (1) $$

The deuterium tritium reaction is accompanied by the release of enormous energy and the formation of a fast neutron. However, its implementation requires an ultrahigh temperature T = 10^7–10^8 K and enormous compression (implosion). In addition, reagents are needed: heavy hydrogen isotopes – deuterium and tritium. The ingenious "explosive" was proposed back in 1949 by Vitaly Lazarevich Ginzburg: lithium-6 deuteride (**^{6}LiD**). It is a solid that can be layered in a hydrogen

bomb body. If the trigger is detonated (a small atomic bomb in the same casing) then ultrahigh temperatures and implosion of explosives will be the result.

$$^{6}_{3}\mathrm{Li}+^{1}_{0}\mathrm{n} \rightarrow {}^{3}_{1}\mathrm{H}+^{4}_{2}\mathrm{He}+\mathrm{E}_{1}\,, \quad \text{where } \mathrm{E}_{1}=4.8\ \mathrm{MeV}_{\text{synthesis}}. \qquad (2)$$

The neutron flux will cause a tritium reaction and then the tritium will react with deuterium according to (1). These are the formulas for the formation of explosion energy. However, the topic of the article is to recall the achievements in chemistry and technology of lithium-6 and deuterium. In nature, there are two stable lithium isotopes: ^{6}Li (7.5%) and ^{7}Li (92.5%). During SAP, mercury technology was used to obtain pure ^{6}Li. To obtain deuterium, an effective and economical technology for low-temperature rectification of liquid hydrogen [17] was developed at the Institute of Physical Problems of the USSR Academy of Sciences under the leadership of Anatoly Petrovich Aleksandrov. The author of the idea of technology and the creator of the cryogenic Petr Leonidovich Kapitsa at that time was removed from the leadership of the institute. Highly appreciating each other's contributions, they both refused the Lenin Prize for this work, giving everything to the Institute of Physical Problems.

The technology for producing tritium according to (2) not in a bomb, but in terrestrial conditions, for the first thermonuclear charge was developed at *NII-9* beginning in 1950 under the guidance of K.A. Bolshakov in Z.V. Ershova's laboratory [18-20]. And today, after the completion of SAP, the technology for processing ceramic products from lithium-6 irradiated inside a reactor with the aim of producing tritium is used at the Mayak plant to produce the main fuel component of the international thermonuclear experimental reactor (ITER) under construction in France.

Conclusion

The brief overview of the implementation of the Soviet atomic project convincingly shows the significant contribution of SAP to the chemistry and technology of isotopes of the lightest and heaviest chemical elements of the Mendeleev Periodic Table.

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