

# THE CONTRIBUTIONS OF RADIOCHEMISTRY TO MASTERING ATOMIC ENERGY FOR WEAPONS

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## Introduction

In 1945, mankind entered into the era of practical use of atomic energy—the atomic age. During the Second World War, American and European scientists, engineers, craftsmen, and laborers created the nuclear industry in the USA leading to the manufacture, in 1945, of the first finished products—nuclear explosives based on the fission of plutonium-239 and uranium-235. In the USSR, 1945 marked the initiation of the nuclear industry which culminated in the first Soviet nuclear explosive, based on plutonium-239, in 1949, and the start-up of the first-ever atomic power station in 1954. Development of the nuclear industry in both countries involved massive contributions by various branches of science—including geology, nuclear physics, radiochemistry, and metallurgy—and all branches of engineering. In the present article, we describe the contribution of radiochemistry to mastering atomic energy and compare and contrast, for the USA and the USSR, the sources of uranium and the first radiochemical technologies in isolation of the plutonium produced by irradiation of uranium and the treatment of the radioactive wastes arising from these separations.

## Role of Radiochemical Technology in Mastering Atomic Energy

The roles of radiochemistry in nuclear industry lie in separation and purification of natural uranium from ores, production of uranium hexafluoride for isotope enrichment, production of uranium- and uranium/plutonium-bearing feeds both as nuclear fuel and as fertile material for irradiation in reactors, isolation and purification of plutonium and uranium from the irradiated uranium, and treatment processes for the resulting radioactive waste (1). The key importance of these processes in building atomic weapons was noted by Edward Teller in a 1962 conference in Seattle, observing that once the nuclear material is acquired, it is only a matter of months until a nuclear explosive can be fashioned (2). According to this authoritative physicist and weapons designer, the most complex and difficult part in mastering atomic energy for atomic weapons production lies not in designing the nuclear explosive but rather creating and implementing the technology to produce the fissionable material— $^{239}\text{Pu}$  and  $^{235}\text{U}$ —in sufficiently high quantities and purity. Of these, plutonium-239 as the ingredient for nuclear explosives is apparently more effective and accessible based on the experience of those states—the USA, USSR, United Kingdom, France, India, North Korea, and Israel (undeclared)—whose first nuclear explosives were based

on plutonium. Only China, Pakistan and (purportedly) South Africa's first nuclear explosives used enriched uranium (3).

The technology of plutonium weapons production consists of neutron transmutation of uranium-238 in reactors, separating plutonium from the uranium and fission products in radiochemical plants, and fashioning the explosive. Of the three steps needed to produce a  $^{239}\text{Pu}$ -based nuclear weapon—the reactor, the separation, and crafting the explosive device—two, the first Soviet industrial reactor for plutonium production and the first Soviet nuclear explosive device, were almost exact copies of the American designs, thanks to receipt of clandestine technical information. However the Soviet radiochemists did not receive comparable detail about the American radiochemical techniques and the plutonium separation plant at Hanford, thus necessitating development of indigenous Soviet separations technology.

### Acquisition of Uranium Raw Materials for the First Nuclear Projects

Uranium ore from the Shinkolobwe mine in the Katanga Province of the Belgian Congo (now the Democratic Republic of the Congo) provided the raw materials for the first successful American and Soviet nuclear explosive efforts and the unsuccessful German efforts (4). This ore was the richest in the world, a unique deposit now exhausted. In the 1930s and 1940s, the Belgian company *Union Minière du Haut Katanga* produced a uranium concentrate of 65%  $\text{U}_3\text{O}_8$ . More than 90% of the world's uranium stockpile in 1939 arose from the Congo and at this time, the company *Union Minière* sent half of its procured concentrate to Belgium with the second half stored in Africa. In August 1939, a month before World War II commenced, Nobel Prize winner Frédéric Joliot-Curie contacted Edgar Sengier, director of *Union Minière*, explained to the Belgian businessman the value of uranium for potential weapons and, on behalf of the government of France and to the exclusion of Germany, offered a contract to buy the entire stock in Belgium and Africa as well as any future uranium production. Sengier, who had earlier refused a similar request by an English representative, agreed to the French contract but the outbreak of World War II prevented completion of the contract. Belgium soon was occupied by German forces who confiscated and removed to Germany 1200 tonnes of uranium concentrate and used it in their unsuccessful nuclear research. At the capitulation of Germany in May 1945, much of the African-Belgian uranium held by the

Germans lay in the American region of occupation and was taken to the USA for nuclear applications.

Meanwhile, the ore concentrates held by *Union Minière* in Africa became the main source of uranium for the Americans' Manhattan Project. With the advent of hostilities in Europe, Sengier, at the advice of Joliot-Curie and unknown to the German occupiers, organized in September 1940 marine transport of uranium concentrates from Africa to the port of New York (in Staten Island) where the concentrate was stored as foreign property nearly two years before the Manhattan Project started in earnest (4). Thus the USA, long before recognizing the need to acquire uranium raw materials, received a unique uranium concentrate not as a military trophy, not as a purchase made in anticipation of future use, but rather through the prescient actions of two Europeans, a critical consignment literally at its doorstep ready for use, subject only to payment. The load contained 1250 tonnes of 65%  $\text{U}_3\text{O}_8$  concentrate and constituted almost half of the world's separated reserve at that time. This quantity, plus the 3000 tonnes as ore stored in the Congo and later retrieved by the Americans, was more than enough for the first reactors and the first American nuclear explosives of both types. This "gift" to the United States made by Edgar Sengier, at the advice of Frédéric Joliot-Curie, reduced the timeline of American atomic weapons development by years as the United States at that time possessed only poor uranium ores and little indigenous uranium mining and milling capability. The USSR requested some kilograms of pure metallic uranium and uranium compounds from the USA in 1943 under terms of the Lend-Lease program. The USA agreed and provided the USSR 20 kg of metallic uranium, 100 kg of uranium oxide, and 220 kg of uranyl nitrate in April 1943, sufficient to supply materials for laboratory studies for the Soviet atomic project (5, p 98).

The Soviet side likewise benefitted from the seizure of about 200 tonnes of the Congolese mining concentrate, acquired after the surrender of Germany in the Soviet zone of occupation (6, p 108). The Soviet effort also benefitted from the existence of rich uranium deposits in Germany's Sudetenland, in the Joachimstal of the "Ore Mountains" (Erzgebirge). These Congolese concentrates and European minerals served as important, but not unique, uranium sources for the first Soviet reactors and for building of the first Soviet nuclear explosives as the production of uranium from Soviet Asiatic deposits increased quickly—from 14.6 tonnes in 1945 to 129.3 tonnes in 1947 and to 278.6 tonnes in 1949 (5, p 192).

The USSR undertook joint enterprises in 1946-1949 with several Central European countries—the German Democratic Republic (GDR), Czechoslovakia, Bulgaria, and Poland—to make significant addition to the atomic project uranium supply. In so doing, Soviet geologists discovered new uranium ore deposits and more precisely defined established deposits thus augmenting the uranium ore reserves in these countries many fold. Rich uranium deposits were found in GDR's Saxony at Johanngeorgenstadt, Schneeberg, and Oberschlema in the Erzgebirge. The most important uranium deposit was Niederschlema-Alberoda and was the main source of uranium for the Soviet-German corporation "Wismut" until the dissolution of the Soviet Union in 1991. The joint Soviet-Czech enterprise at Jáchymov was created to exploit the old mines Rovnost and Svornost and work the new mines Berg Slavkov and Příbram in western and central Czechoslovakia. A joint Soviet-Bulgarian mining enterprise was created based on a known deposit at Goten with new deposits found at Seslavci. Nevertheless the uranium reserve was small in Bulgaria: 16 tonnes at the beginning of 1946 and 163 tonnes by 1950. A joint Soviet-Polish commission and the enterprise "Kowarski Mines" was created in 1947 with several new uranium deposits discovered. As in Bulgaria, these deposits were poor and the total uranium reserve in Poland was small. The Wolność deposit, the richest in Poland, was exhausted in 1952. The total uranium reserve and concentrations in the ore in these four Central European countries were modest compared with those in the Congo, Canada, and other countries utilized by the USA. The early uranium resources available to the Soviet atomic project by indigenous Soviet and joint Soviet-Central European efforts is given in Table 1. The total uranium delivered to the USSR from Central Europe countries in 1945-1949 thus was ~1700 tonnes, a quantity somewhat less than that

available to the USA from Congolese resources at the outset of the Manhattan Project.

### The First Radiochemical Technologies to Prepare High-Purity Plutonium in the USA

The reactor irradiation of uranium is used to produce plutonium for atomic weapons. The most complex and waste-laden part of this technology is the isolation of plutonium from the admixture of uranium and radioactive fission products in the irradiated uranium fuel. To be used in nuclear armaments, the plutonium, which is present in quantities of only hundreds of grams per ton of irradiated uranium, must be purified from these accompanying elements by a factor of greater than  $10^6$  (separation factor).

The initial American isolation technology, applied in 1944 to 1956 at the Hanford Site T and B Plants in Washington state, relied on separate coprecipitation of first plutonium and then fission products using bismuth phosphate. In the first step, Pu(IV) in nitrate solution was separated from U(VI) and most of the fission products by coprecipitation with  $\text{BiPO}_4$ . The plutonium-bearing  $\text{BiPO}_4$  precipitate then was dissolved, the plutonium oxidized to Pu(VI) using Ce(IV) or Cr(VI), and the  $\text{BiPO}_4$  precipitation repeated, this time capturing residual fission products while leaving the Pu(VI) in solution. The dissolved plutonium then was chemically reduced to Pu(IV) and the Pu(IV)/Pu(VI) steps repeated two more times. A similar cycle followed, this time using lanthanum fluoride,  $\text{LaF}_3$ , as the carrier, each time further purifying and concentrating the plutonium. Finally, plutonium was isolated from lanthanum by metathesizing the  $\text{LaF}_3$  carrier in potassium hydroxide solution to remove the fluoride, dissolving the hydroxide cake in acid, and precipitating the plutonium as the Pu(III)/Pu(IV) peroxide while lanthanum remained in solution.

**Table 1.** Uranium ore concentrate production in the USSR and for the USSR from Central European resources, 1945-1949.

Country	Uranium Production, tonnes				
	1945	1946	1947	1948	1949
USSR	14.6	50.0	129.3	182.5	278.6
GDR (East Germany)	–	15.7	150.0	321.2	767.8
Czechoslovakia	–	18.0	49.1	103.2	147.3
Bulgaria	–	26.6	7.6	18.2	30.2
Poland	–	–	2.3	9.3	43.3

From pp 192 and 197 in Ref. 5.

Edwin McMillan and Philip H. Abelson (Figure 1) in 1940 used an oxidation-reduction coprecipitation cycle of purification in the isolation and discovery of neptunium, the first transuranium element, prepared by bombarding uranium with neutrons using Ernest O. Lawrence's 60-inch cyclotron (7). Stanley Thompson and Glenn Seaborg (Figure 2) adapted this coprecipitation concept to plutonium isolation and patented the  $\text{BiPO}_4$  portion of the plutonium separation process that used a similar oxidation-reduction coprecipitation cycle (8). The choice of bismuth phosphate as the carrier

was fortuitous and unexpected even for its inventors (9). The Seaborg research group, located at the Metallurgical Laboratory at the University of Chicago, investigated many candidate carriers for plutonium including the nearly insoluble phosphates of zirconium, niobium and thorium, as well as sodium uranyl triacetate as used by McMillan and Abelson for neptunium isolation and identification. Various advantages and disadvantages were found in these investigated carriers. For example, sodium uranyl triacetate carried plutonium but formed small crystals that filtered slowly.



**Figure 1.** Edwin McMillan (left) and Philip Abelson (right), co-discoverers of neptunium. Photo taken in the Berkeley 60-inch cyclotron magnet, September 1938. E. O. Lawrence is seated in the front row, middle, and Robert Oppenheimer is standing in the top row, middle, above Lawrence. Photo XBD9706-02525 courtesy Lawrence Berkeley Laboratory, Berkeley, CA, USA (henceforth LBL).



**Figure 2.** Stanley Thompson (left) and Glenn Seaborg at centrifuge in 1948. Photo XBD9704-01812 courtesy LBL.

It was Thompson (Figure 3), Seaborg's high school

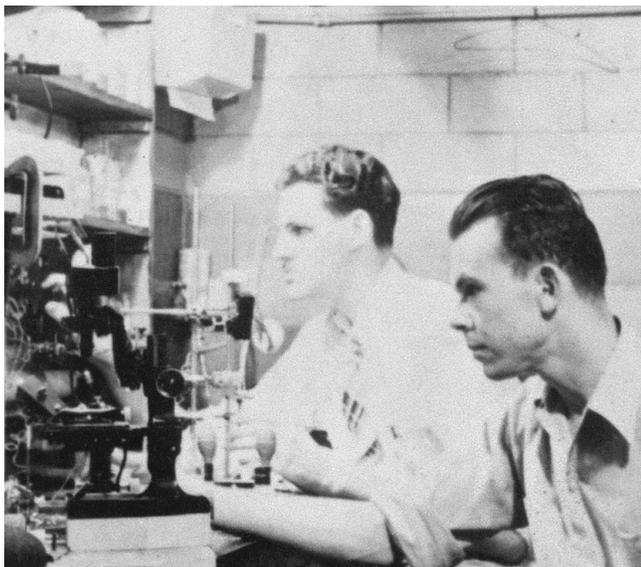
and college classmate, invited by Seaborg to join the Metallurgical Laboratory, who suggested trying  $\text{BiPO}_4$  as a carrier. Thompson knew this carrier as a filter aid from his prior job at Standard Oil. In his testing, Thompson noted that  $\text{BiPO}_4$  satisfied many requirements for plutonium separation—it is almost insoluble in dilute nitric acid but readily soluble in concentrated nitric acid, it forms large, quickly-settling, and readily-filtered crystals, and the accompanying phosphate retards steel corrosion thereby saving process equipment and minimizing plutonium product contamination. Of course, nothing initially was known about the ability of bismuth phosphate to coprecipitate plutonium in its different oxidation states. Thompson and Seaborg predicted that  $\text{BiPO}_4$  would coprecipitate  $\text{Pu}^{3+}$  by its substitution for  $\text{Bi}^{3+}$  but considered improbable that  $\text{BiPO}_4$  would trap  $\text{Pu}^{4+}$ , the most stable plutonium valence in nitric acid solution. Nevertheless,



**Figure 3.** Stanley G. Thompson, co-discoverer, with Glenn Seaborg, of the bismuth phosphate process. Photo taken 20 February 1950. Photo XBD200912-01073 courtesy LBL.

bismuth phosphate was included for investigation. Using ultramicrochemical techniques involving only tens of micrograms of plutonium, Thompson (Figure 3), with Burris Cunningham and Louis Werner (Figures 4 and 5), carefully investigated plutonium coprecipitation, in its various oxidation states, with  $\text{BiPO}_4$  and found in the period 19 December 1942 to 29 March 1943 that  $\text{Pu}^{4+}$  is indeed carried with high efficiency (10, pp 223-224 and 258-259) using the uranium concentrations and ~100:1 Bi:Pu ratios corresponding to those envisioned

in the full-scale separation plant (8, Table I). At the same time, Pu(VI), as  $\text{PuO}_2^{2+}$ , was found not to be captured by  $\text{BiPO}_4$ . Plutonium(V) (as  $\text{PuO}_2^+$ ), the other potential oxidation state in solution, does not exist in appreciable concentrations above about 0.4 M  $\text{HNO}_3$ .



**Figure 4.** Louis B. Werner (left) and Burris B. Cunningham (right), early developers of the bismuth phosphate process. Photo taken at the Metallurgical Laboratory, Chicago. Photo XBD9611-05594 courtesy LBL.



**Figure 5.** Burris B. Cunningham demonstrating ultramicrochemical techniques used in early plutonium chemistry investigations at the Metallurgical Laboratory, Chicago. Courtesy LBL.

Thus the new carrier met the desired process requirements (9). Even though separations from the numerous fission products were incompletely known, DuPont, the Hanford Site engineering firm, proceeded on 7 June 1943 with plant construction on these bases using an ingeniously flexible design (10, p 284). However there remained the concern of scale, multiplying the Metallurgical Laboratory  $\text{BiPO}_4$  findings done using tens-of-micrograms of plutonium by a factor of  $\sim 10^7$  to reach hundreds-of-grams batch sizes for the Hanford Site T, B, and U Plants being constructed by DuPont (9). The construction and operation of the plutonium separation plant using  $\text{BiPO}_4$  technology thus represented a bold calculated risk. As was stated in the official 1945 American report on the Manhattan Project (11, paragraph 7.3):

In peacetime, no engineer or scientist in his right mind would consider making such a magnification in a single stage, and even in wartime only the possibility of achieving tremendously important results could justify it.

Seaborg assured DuPont that even incomplete plutonium capture by  $\text{BiPO}_4$  still would provide sufficient yield. Although  $\text{BiPO}_4$  was the favored initial coprecipitation agent, the selection of  $\text{BiPO}_4$  process parameters, the subsequent  $\text{LaF}_3$  cycle parameters, and the final segregation as plutonium peroxide awaited verbal confirmation by Seaborg to Du Pont plant authorities in a visit to Hanford in 13-15 December 1944. By this time, Thompson had transferred to Hanford to lead the Process Research Group in the Process Chemistry Section (10, pp 576-580). In fact, the initial plutonium separation operations occurred in T Plant on 9 December 1944, before Seaborg's verbal confirmation, using uranium metal slugs irradiated in the Clinton Laboratory (Oak Ridge) X-10 reactor supplemented by non-irradiated slugs (12). The second T Plant run, using a less-than-full charge of uranium metal fuel slugs lightly irradiated in Hanford's B Reactor, supplemented by non-irradiated uranium, occurred on 14 December 1944 while the flowsheet discussions were in progress (Figure 6). Both were "tracer studies" in that the first contained milligram quantities of plutonium product and the second only gram quantities (13). The completeness of extraction gradually exceeded design norms, beginning at 60-70% in the first two months, 90% in the third, 93% after six months, and then above 95% with decontamination factors of  $10^8$  (14). This success was due to the fortuitous and non-intuitive discovery of the  $\text{BiPO}_4$  carrier and the creativity and persistence of the American radiochemists. It is noteworthy that, in contrast to the Manhattan Project efforts in reactors and nuclear explosives, whose discoveries were led and fostered in

key areas by European refugees (e.g., Enrico Fermi, Leo Szilard, Hans Bethe, John von Neumann, James Franck, Edward Teller, Rudolf Peierls, George Kistiakowsky), the key radiochemical separation innovations were solely products of US-born contributors.



**Figure 6.** T Plant, Hanford, based on bismuth phosphate coprecipitation (long building at center) and lanthanum fluoride (building at the left), operated 1944-1956. Photo taken 22 December 1944, during initial start-up operations. Taken from archival original of Ref. 15.

### The First Radiochemical Technologies to Prepare High-Purity Plutonium in the USSR

The initial separations of plutonium from irradiated uranium took place in the Soviet Union on an industrial basis under the scientific direction of Vitaly G. Khlopin (Figure 7), Academician from the Academy of Sciences of the USSR, director of the Radium Institute in Leningrad (now Saint Petersburg), and scientific head in development of the first radium production in the USSR (16). The first Soviet plutonium was produced in industrial scale at the B Plant of Complex 817, now Mayak, at the town of Ozyorsk, Ural, Chelyabinsk Region, using acetate-fluoride coprecipitation technology (17, 18, 19). The plutonium carriers were sodium uranyl triacetate  $[\text{NaUO}_2(\text{CH}_3\text{CO}_2)_3]$  followed, like the American plutonium separation process, by  $\text{LaF}_3$ . Each of these agents was used as published earlier by McMillan and Abelson (7) in the discovery and isolation of neptunium, but using  $\text{LaF}_3$  in place of  $\text{CeF}_3$ .

In the Soviet process, the irradiated uranium metal was dissolved in nitric acid, the plutonium oxidized to Pu(VI) by dichromate and the Pu(VI) coprecipitated with U(VI) as  $\text{NaUO}_2(\text{CH}_3\text{CO}_2)_3$ . Soluble fission products and process impurities (e.g., spent chromium, corrosion



**Figure 7.** Left: Academician V. G. Khlopin (1890-1950). Scientific director of plutonium separations at Mayak. Middle and Right: Corresponding Member B. A. Nikitin (1906-1952) and Professor A. P. Ratner (1906-1956), developers of the sodium uranyl acetate and lanthanum fluoride processes for plutonium isolation. All were from the Radium Institute of the USSR Academy of Sciences.

products) were rejected with the plutonium-denuded solution. An oxidation-reduction cycle of purification ensued—the  $\text{NaUO}_2(\text{CH}_3\text{CO}_2)_3$  solids with the coprecipitated Pu(VI) were dissolved, the Pu(VI) reduced to Pu(IV), and  $\text{NaUO}_2(\text{CH}_3\text{CO}_2)_3$  again precipitated, leaving the Pu(IV) in solution but  $\text{NaUO}_2(\text{CH}_3\text{CO}_2)_3$  solids, destined for separate uranium recovery, carrying much of the remaining fission products. After this cycle, Pu(IV) was coprecipitated with  $\text{LaF}_3$ . The B Plant at Mayak (Figure 8) began operations on December 1948, exactly four years after start-up of Hanford's T Plant, by the successful dissolution of irradiated uranium fuel. However, initial plutonium recoveries within the analyzed solids and solutions were low.



**Figure 8.** Plant B in Chelyabinsk-40, based on acetate-fluoride technology, operated 1948-1960.

To locate the plutonium, a brigade led by the developers of the technology including Corresponding

Member of the USSR Academy of Sciences, Boris A. Nikitin, and Professor Alexandr P. Ratner, both of the Radium Institute, was engaged (Figure 7). Little by little, the causes of the small plutonium recoveries were found and eliminated. Sorption of dissolved plutonium and solid plutonium deposits on walls and pipelines within the plant appear to have been among the causes for the low yields. Technological process parameters were adjusted, such that with each succeeding dissolved irradiated uranium batch the yield increased until, by April 1949, design norms were reached (17, 19). Work to initiate and then adjust operations in the acetate-fluoride technology was conducted under extreme radioactive exposure. Despite these hazards, the staff worked selflessly such that many received massive doses during the start-up of B Plant. Included in these staff were the process developers. Physicians were not able to thwart development of radiation sickness for Nikitin and Ratner and they died 3 and 6 years after B Plant start-up at the ages of 46 and 49 years, respectively.

It is noted that, along with the acetate-fluoride technology, the USSR scientists considered other plutonium separation methods, including solvent extraction (17, 18, 19). However, only after acetate-fluoride technology began achieving reliable yields did research cease into alternative technologies using diethyl ether as an extractant in Building 102 of the B Plant. Efforts to perform the next chemical step, namely, finishing the separated plutonium into its metallic form at Mayak's C Plant, were led in collaboration by Iliya I. Chernyaev of the Institute of General and Inorganic Chemistry, Anna D. Gelman of the Institute of Physical Chemistry, and Vsevolod D. Nikolsky of the Bochvar Institute (Figure 9). The Cold War necessity to rapidly build atomic weapons, guided by the sense of debt and patriotism, led to willing neglect of safety norms. Thus, the first minister of the Soviet nuclear industry, Vyacheslav A. Malyshev, died early, motivated, with other technological leaders and employees of the nuclear branch, to intentionally run risks to accelerate the work.

### Comparing the USA and USSR Radiochemical Technologies

As this account shows, the first American and Soviet plutonium separation radiochemical technologies were similar in exploiting the differences of plutonium oxidation state properties by coprecipitation but were not identical in the primary carrier selected. Thus, the initial



**Figure 9.** Left: Academician I. I. Chernyaev, Institute of General and Inorganic Chemistry, USSR Academy of Sciences. Middle: Professor A. D. Gelman, Institute of Physical Chemistry, USSR Academy of Sciences. Right: Doctor of Chemical Sciences V. V. Nikolsky, Bochvar Institute of Inorganic Materials (Institute-9). All worked in devising processes to convert and finish plutonium to metal at C Plant, Mayak, 1949.

separation at Hanford used Pu(IV) carried by  $\text{BiPO}_4$  whereas Pu(VI) carried by  $\text{NaUO}_2(\text{CH}_3\text{CO}_2)_3$  was used at Mayak. It is noted that the Americans also investigated  $\text{NaUO}_2(\text{CH}_3\text{CO}_2)_3$  as a carrier for plutonium separation but, having met with large technical difficulties, including waste neutralization, at the Clinton (Oak Ridge) pilot plant, considered this technology unpromising and chose bismuth phosphate technology. The "Smyth Report" alluded to the separation method choices available to the Manhattan Project but was written elliptically, in the style of Aesop, to avoid, in the interest of military secrecy, concrete statements about specific methods and carriers for plutonium separation except to say that several separation technologies were considered (including volatility, absorption, and solvent extraction) and that, in the end, two coprecipitation processes were involved that took advantage of differences in Pu(IV) and Pu(VI) behaviors (11, paragraphs 8.20-8.26).

Although the Soviet Union (and the world) were aware that coprecipitation processes relying on oxidation state changes were used at Hanford to isolate plutonium, the specific agents, including the primary extraction and subsequent decontamination achieved with high efficiency by bismuth phosphate, were unknown to the Soviet technical leaders through open sources and even, evidently, by espionage at the inception of the Soviet B Plant design. As it was, plutonium recovery by coprecipitation with  $\text{BiPO}_4$  was investigated in December 1945 by a group led by Corresponding Member Alexandr A. Grinberg, a professor of the Radium Institute and Corresponding Member of the Academy of Sciences of the USSR since 1946. However, under Khlopin's direction, this approach apparently was judged inferior to the acetate-fluoride technologies.

The coprecipitation of Pu(VI) with  $\text{NaUO}_2(\text{CH}_3\text{COO})_3$  proceeds by isomorphous co-crystallisation, wherein  $\text{PuO}_2^{2+}$  ions readily substitute for  $\text{UO}_2^{2+}$  ions in the bulk crystal lattice. Because of their isomorphism, capture of Pu(VI) by the uranyl compound precipitate is high at any initial Pu:U solution ratio. In contrast, the coprecipitation of Pu(IV) with  $\text{BiPO}_4$  proceeds by anomalous mixed-crystal formation wherein the  $\text{Pu}^{4+}$  and  $\text{Bi}^{3+}$  ions occupy different places in the  $\text{BiPO}_4$  crystal lattice. It is known for such cases that the microcomponent (Pu) capture by the bulk ( $\text{BiPO}_4$ ) precipitate is incomplete if the microcomponent concentration exceeds some critical value. Therefore, the radiochemists of Radium Institute doubted the effectiveness of the  $\text{BiPO}_4$  carrier at higher plutonium concentrations. Furthermore, the USSR lacked bismuth production capability (17). The Radium Institute directorate and the Soviet atomic project leadership approved use of the  $\text{NaUO}_2(\text{CH}_3\text{CO}_2)_3$  and  $\text{LaF}_3$  coprecipitation technologies noting that they provided not only purified plutonium but also recovered the uranium for future isotope enrichment (17).

### Radiochemical Treatment Technologies for High-Level Liquid Wastes in the USA and USSR

The American and Soviet/Russian radiochemical plutonium technologies have appreciable differences in radiochemical high-level liquid waste (HLLW) management (20) but some interesting similarities. The big advantage of American plutonium separation technology was that the first Pu(IV) coprecipitation with  $\text{BiPO}_4$  yielded only kilograms of precipitate for further processing from each 1 to 1.5-tonne uranium metal batch, not tonnes as was the case with the Soviet  $\text{NaUO}_2(\text{CH}_3\text{CO}_2)_3$  process which handled all of the uranium with the plutonium in the first plutonium separation step. At Hanford, the uranium- and fission product-bearing mother solution obtained after the first  $\text{BiPO}_4$  precipitation could be disposed as high active waste for later uranium recovery. Ensuing  $\text{BiPO}_4$  and  $\text{LaF}_3$  precipitations further decontaminated the plutonium of uranium and fission products but yielded only kilograms of waste.

At Mayak, each of the five sodium uranyl triacetate precipitations yielded many cubic meters of high-level liquid wastes or HLLW (1). As a result, Mayak's acetate technology produced perhaps 10 to 20 times more uranium-specific HLLW volume than Hanford's bismuth phosphate technology, the volumes of the latter being initially 64 liters per kg of uranium and decreasing to 20

liters per kg through process improvements. However, the Soviet technology separated both weapon plutonium and purified uranium as feed for isotopic enrichment whereas the American bismuth phosphate technology yielded only purified plutonium. Subsequent recovery of the valuable uranium contained in the waste from the first  $\text{BiPO}_4$  precipitation at Hanford occurred in the 1950s by sluicing waste from the tanks, dissolving the uranium-bearing solids in nitric acid, and tributyl phosphate solvent extraction, separation and purification.

For a variety of reasons, American HLLW treatment differed in other ways from that of the Soviet methods. First, the American nitrate waste chemical composition strongly differed from the high-salt nitrate-acetate Soviet waste. At Hanford, the acidic nitrate liquid wastes were made alkaline by addition of  $\text{NaOH}$  so that they could be disposed into mild steel-lined underground storage tanks. The Americans also evaporated water from the wastes, both by radiolytic heating and by applied external heat, to decrease waste volume. Although corrosion was expected to be low for the mild steel in contact with the alkaline waste, stress corrosion, the effects of chemical combination and thermal stresses, perhaps accelerated by radiolysis, caused leaks to occur in the steel liners of these concrete tanks, allowing waste solutions to enter the underlying Hanford sand and gravel.

A total of 177 underground tanks were built to store these wastes (now totaling  $\sim 200,000 \text{ m}^3$  waste volume), 149 of nominal 20-year lifetime constructed 1943 to 1964 and having a single steel lining within concrete. Beginning in 1968, 28 double-shell (steel) tanks within concrete having a 50-year projected lifetime were constructed. The first confirmation of single-shell tank leakage occurred in 1959, and many more have been confirmed since then (21). Solutions present in the single-shell tanks have been moved to the more secure double-shell tanks. One of the double-shell tanks was recently discovered to have leaked into its annulus but with no confirmed leakage past the second shell into the surrounding soils. Billions of dollars have been spent and will continue to be spent until the waste is removed from the tanks and rendered into more stable forms including glass (22). Meanwhile, extensive characterization of these wastes has been undertaken, including studies of the disposition of plutonium, aided by contributions from French and Russian as well as USA scientists (20, 23).

Neutralization of the first industrial HLLW in Russia at Mayak proceeded more dramatically. The technology of neutralization was developed in laboratory scale in 1949 by members of the Institute of Physical Chemistry

(IPC) of the Soviet Academy of Sciences. However, it was not utilized at Mayak because the B Plant liquid wastes contained salts (sodium acetate and sodium nitrate,  $\text{NaCH}_3\text{CO}_2$  and  $\text{NaNO}_3$ , respectively) and potassium dichromate at higher concentrations than were stated in the detailed design and studied in the laboratory (19, 20). The evaporators designed to reduce HLLW volumes could not function because of salt loading and aggressive equipment corrosion caused by radiation and the high concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$  used to oxidize plutonium to Pu(VI). As a result, the B Plant HLLW volume surpassed the waste tank capacity in 1949.

To address this waste storage problem, either replacement of the sodium uranyl triacetate process had to be implemented, production of plutonium stopped, or an alternative means found to handle the waste. The decision to this problem was made in the crucible of the Cold War and the perceived threat of ~200 atomic weapons in the USA arsenal deliverable by air from military bases in countries surrounding the USSR. Under these conditions, the Soviet nuclear design leadership demanded that plutonium production continue and means found to process the B Plant HLLW. Only one option was possible—shunt the HLLW to the Techa River and to adjacent reservoirs such as Lake Karachay.

This expedient was a serious and ecologically dangerous extrapolation of the initial design which called for disposal of only low-level liquid wastes to the Techa River. A commission to ameliorate the ecological effects included representatives of leading research institutes: Corresponding Member Iossef E. Starik (Radium Institute), Corresponding Member Simon Z. Roginsky (IPC; Figure 10), the head of Public Service of Radiation Safety of the USSR, Avetik I. Burnazian, Academician A. P. Aleksandrov (director of the Institute of Physical Problems, Academy of Science), and Corresponding Member Alexandr P. Vinogradov (Institute of Geochemistry, Academy of Sciences). The commission was forced to recommend disposal to the Techa River but to minimize the ecological effect by pre-disposal adjustment of the HLLW to neutral pH and dilution to the maximum possible extent.

Simultaneously in 1949, the design management transferred Corresponding Member Viktor I. Spitsyn from the Lomonosov Moscow State University to deputy director of the IPC as supervisor of waste neutralization studies. From the end of 1949 until the beginning of 1951, Spitsyn, with Neonila E. Brezhneva and Boris A.



**Figure 10.** Top left: Corresponding Member S. Z. Roginsky (1900-1970). Top right: Candidate of chemical sciences N. E. Brezhneva, future doctor of sciences and the winner of the Lenin Award (on left) and Corresponding Member V. I. Spitsyn, elected Academician in 1958 (on right). Bottom: Sergeant, and future doctor of chemistry and winner of the Lenin award B. A. Zaitsev (on the left) with fellow soldiers in the Soviet army, Germany, 1945. All were radiochemists of the IPC of the USSR Academy of Sciences active in devising processes for radioactive waste neutralization and decontamination for Mayak.

Zaitsev (Figure 10), developed methods to decontaminate HLLW by carrier precipitation using nickel ferrocyanide (primarily for radioactive cesium) and the oxyhydroxides and sulfides of iron and nickel (primarily for radioactive strontium and rare earths). The settled solids occupied <1% of the initial HLLW solution volume. These coprecipitation schemes were implemented at B Plant to produce sludges of small volume that were stored successfully in stainless steel tanks for more than 50 years and allowed discharge of the decontaminated solutions. Vitrification of this “historical” waste sludge commenced at Mayak at the beginning of the 21<sup>st</sup> century. Based on nearly contemporaneous research at Mound Laboratory (24), Hanford likewise independently embarked on a very similar program in 1954-1958, and for very similar purposes, to decontaminate the Hanford T and B Plant waste solutions so that they could be discharged to the environment, as well as for uranium recovery. In this case, discharge was underground to the dry sand/gravel

above the water table, leaving the precipitates in the waste tanks, and freeing the tank waste volume associated with the liquids. As at Mayak, the cesium was removed using nickel ferrocyanide. Strontium was removed by dilution with calcium and nonradioactive strontium nitrates and precipitation as the corresponding sulfates and phosphates (25).

It is interesting to note that the storage times and resolutions of these problematic “historical” HLLW from both the Hanford and Mayak technologies have required incubation times of a half-century! This delayed outcome was a consequence of the fact that, at the beginning of the nuclear industry, both in the USA and the USSR, basic attention was given to plutonium production for nuclear arms while radioactive waste treatment was accorded secondary importance. This singlemindedness is apparent by the following example. In 1949 in the USSR, plutonium science and technology occupied tens of thousands of workers in various scientific research institutes and operations sites. At the same time, radioactive waste management was addressed by only one institute. That institute was the IPC, a department of 30 employees, including technicians and scientists devoted to waste management for industrial Complex 817. Only after 1949 did similar research groups arise in other scientific Soviet organizations including the Radium Institute and Bochvar Institute of Inorganic Materials.

### Later Developments in Plutonium Separations

Despite the successful experience of the T (and duplicate B) Plants based on bismuth phosphate in Hanford in 1944-1956, plutonium separation was supplemented, in 1951, by solvent extraction by the more effective REDOX process, using methyl isobutyl ketone solvent extraction and then succeeded in 1956 by the PUREX process using tributyl phosphate diluted in kerosene for solvent extraction (26). The PUREX process is now the worldwide baseline plutonium and uranium separation technology for irradiated fuel. The rapid early evolution of plutonium separation technologies in the USA may be contrasted with the extended use of coprecipitation technology in the USSR. The B Plant at Mayak used acetate-fluoride coprecipitation technology from 1948 until 1960. An improved acetate technology conducted without the succeeding  $\text{LaF}_3$  steps was used in the DB (double B, or BB) Plant at Mayak with implementation delayed until 1959 because of an HLLW explosion in 1957 (17). The DB Plant successfully operated more than

15 years (19). As the acetate technology was improved, a new unique one-cycle extraction technology to separate weapon plutonium from irradiated uranium was developed based on the PUREX Process. This new technology was tested and introduced into commercial operation at Mayak in 1976 (19). This plant ceased operation in 1989 as an outcome of treaties concluded between the USSR and the USA.

However, the improved acetate technology endured in the USSR until the 1980s (27, 28). One important cause of its longevity was the successful and inexpensive solution of HLLW disposal implemented at the Tomsk Siberian Chemical Combine (SCC) and Krasnoyarsk Mining Chemical Combine (MCC). Through joint efforts of geologists of the Siberian Territorial Management of the Ministry of Geology, radiochemists of the IPC of the Academy of Sciences, specialists from project institutes of the Ministry of Atomic Energy, and employees of the SCC and MCC, a method of underground HLLW injection into clay bed strata at depths greater than 180 m was implemented (27, 28). Russian geologists forecast that the radioactive waste disposed in these isolated layers near the SCC and MCC will remain fixed for many millions of years, sufficient to decay even the longest-lived waste radionuclides. The forecast takes into account the absence of volcanic activity, earthquakes, and significant geological shearing over the past millions of years in the Siberian region of the SCC and MCC. Nevertheless, monitoring for radioactive contamination in observation boreholes around the underground radioactive waste location will be necessary for many years. In contrast, the underground layers in the Ural region near Mayak do not have these favorable attributes for immobilizing HLLW. Therefore, at Mayak, the HLLW treatment method is incorporation into phosphate glass. Large-scale use of underground in-situ HLLW disposal at the SCC and MCC complexes in Siberia has avoided radioactive environmental contamination and considerably reduced capital and operational expenses compared with vitrification and repository storage. These two Siberian industrial complexes' half-century of experience in deep geologic liquid radioactive waste disposal has confirmed the projected reliability and environmental safety of this disposal method (20).

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