

THE FIRST NUCLEAR REACTOR, THE PRODUCTION OF PLUTONIUM AND ITS CHEMICAL EXTRACTION

by

Glenn T. Seaborg

CHAIRMAN, US ATOMIC ENERGY COMMISSION

This Special Number of the Agency Bulletin commemorates the 20th anniversary of the operation of the first nuclear reactor at the Metallurgical Laboratory of the University of Chicago on 2 December 1942. Although this first experiment is generally considered to mark the beginning of the atomic age, it had at that time a single objective. This was to show the feasibility of manufacturing in quantity the new element, plutonium, through the demonstration of a nuclear chain reaction operating with natural uranium.

With the feasibility of such a nuclear reactor thus demonstrated, two outstanding questions still remained. One involved the problem of building such a nuclear reactor, operating on natural uranium, for operation at such a high power level that sufficient quantities of plutonium could be produced within the required short time scale. The other question was whether it would be possible to devise, also within the required short time interval, the chemical means for separating this plutonium from the uranium and from the tremendous quantities of fission product radioactivities that would be present.

These were the two very difficult problems which formed the basis for the American Plutonium Project. Their solutions were, in large measure, unrelated, and the development programme in each case was in the hands of research men in different fields, namely physics and chemistry.

The present account will be concerned with only the second of these problems, that is, the development of the processes for the chemical separation and purification of the plutonium. Fortunately, this task was undertaken against a background of a considerable amount of previous chemical investigation of this element.

Plutonium had been discovered nearly two years earlier and a great deal of investigation of its chemical properties had already taken place. Plutonium was discovered in experiments extending from December 1940 into January and February of 1941, as a result of the production and chemical identification of the isotope with the mass number 238 resulting from the bombardment of uranium with deuterons in the 60-inch cyclotron at the University of California at Berkeley. The fissionable isotope of



Glenn T. Seaborg

plutonium, plutonium-239, production of which formed the objective of the Plutonium Project, was discovered early in 1941, as a result of bombarding natural uranium with the high flux of neutrons produced through the use of the same 60-inch cyclotron. The fact that it is fissionable with slow neutrons was first demonstrated on 28 March 1941, with neutrons produced through the use of the 37-inch cyclotron, also in the Radiation Laboratory of the University of California at Berkeley. This established the great value of this isotope for the release of nuclear energy.

The chemical properties of plutonium were then studied by the tracer method at the University of California for the next year or so, using chiefly the isotope plutonium-238. On the basis of these experiments, it was established that plutonium has at least two oxidation states, the lower of which has chemical properties much like those of the rare earth

ions, and the upper of which has chemical properties much like those of the uranyl ion. In addition, it was established that the higher oxidation state could be obtained by treatment of the lower state with oxidizing agents such as persulphate and argentic ions, dichromate, permanganate, or periodate ions, and that the upper state could be reduced to the lower state by treatment with such reducing agents as sulphur dioxide or bromide ion. It was demonstrated that plutonium in the lower oxidation state was carried by such compounds as the rare earth fluorides, but was soluble in the presence of rare earth fluorides in the upper oxidation state. On the basis of these experiments, the principle of the oxidation-reduction cycle was conceived - a principle which was to form the basis of the chemical processes to be developed later in the Plutonium Project.

When the scientists in the various fields were assembled at the Metallurgical Laboratory early in 1942, and the responsibility for developing the chemical separation process was assigned to the chemists and chemical engineers, this early work at Berkeley formed the basis for these efforts. Among the possible separation procedures that were investigated during these first months at the Metallurgical Laboratory were precipitation, solvent-extraction, volatility, adsorption-elution, and pyrometallurgical and pyrochemical processes. As a matter of fact, all of the types of chemical processes now in use in plutonium manufacturing plants, or under investigation for such use, were included in this early scouting programme of the year 1942. It was decided before the end of 1942 to use a precipitation process because this seemed to offer the greatest certainty of at least limited success in the short time interval involved, even though it did not seem to offer the greatest ultimate efficiency and would not lead to the recovery of the uranium for re-use.

The problem which had to be solved was that of developing a process which would separate plutonium in high yield and purity from many tons of uranium in which the plutonium was present at a maximum concentration of about 250 parts per million. Because of this low concentration, compounds of plutonium could not be precipitated; thus any precipitation separation process had to be based on coprecipitation phenomena, i. e. the use of so-called "carriers" for plutonium. In addition, the radioactive fission products which are produced along with plutonium in the uranium (as a result of the fission of U^{235}) had to be separated so that less than one part in 10^7 parts originally present with the plutonium would exist with the final product from the process. This requirement was necessary in order to make it safe to handle the plutonium, because without a separation of the fission products, the plutonium from each ton of uranium would have more than 10^5 curies of energetic gamma radiation associated with it. The process of removing fission products is called "decontamination". A unique feature of the process was,

therefore, the necessity of separating a wide variety of elements completely from the plutonium and of accomplishing these separations by remote control behind large amounts of shielding in order to protect operating personnel from the radiation hazard.

Although it was felt that the use of the two oxidation states of plutonium, which had been discovered during the early work at the University of California, would be the basis for the separation process, the details such as the best carrier compounds and best oxidizing and reducing agents had not yet been discovered. The quantitative carrying of plutonium (IV) from acid solution by bismuth phosphate, an unexpected phenomenon which was discovered in December 1942, together with the expected non-carrying of plutonium (VI) by the same carrier material, was the key to the process. This method, the Bismuth Phosphate Process, was operated as follows: neutron-irradiated uranium was dissolved in nitric acid, and, after the addition of sulphuric acid to prevent the precipitation of uranium, plutonium (IV) was coprecipitated with bismuth phosphate. The precipitate was dissolved in nitric acid, the plutonium (IV) was oxidized to plutonium (VI), and a by-product precipitate of bismuth phosphate was formed and removed, the plutonium (VI) remaining in solution. After the reduction of plutonium (VI) to plutonium (IV), the latter was again coprecipitated with bismuth phosphate, and the whole "decontamination" cycle was repeated. The carrier was then changed to lanthanum fluoride, and a similar oxidation-reduction cycle was performed to achieve further decontamination and concentration. Final isolation was accomplished at this point without the use of carrier compounds through the precipitation of plutonium peroxide from acid solution.

The Bismuth Phosphate Process was developed in a remarkably short time. Plutonium was discovered in December 1940, and a plutonium compound was first isolated in August 1942. The properties of bismuth phosphate as a carrier for plutonium were discovered in December 1942, and the Bismuth Phosphate Process was placed in successful operation in the pilot plant at Clinton Laboratories in Tennessee in December 1943. Thus in less than one year, before the total quantity of plutonium produced in cyclotron bombardments had reached two milligrams, the process development work was almost completed. Operation of the large chemical processing plants at Hanford, Washington, began in December 1944. In all, only four years elapsed between the discovery of plutonium and its first isolation in quantity. This accomplishment required not only tremendous financial resources, engineering and chemical skill, careful planning and organization, high priorities for material, skilled manpower and construction facilities, but also imagination and a considerable measure of good fortune.

Although the outline of a chemical separation process could be obtained by tracer-scale investi-

gations, the process could not be defined with certainty until study of it was made possible at the actual concentrations of plutonium that would exist in the large-scale separation plants. Such a test was particularly necessary in view of the poor understanding of the mechanism by which plutonium (IV) is carried by bismuth phosphate and the scepticism of many that the carrying would be observed at the concentrations of plutonium that would exist in the Hanford plant. This test had to be carried out as soon as possible after the discovery of the Bismuth Phosphate Process, and it was performed at the Metallurgical Laboratory in early 1943, following the isolation of plutonium the previous fall. This test was carried out successfully despite the fact that only microgram quantities of plutonium were available, by working on the so-called ultramicrochemical scale. The microgram quantities of plutonium-239 were produced through the irradiation of huge quantities of uranium with the neutrons from cyclotrons.

This ultramicrochemical test of the Bismuth Phosphate Process followed the first isolation of plutonium at the Metallurgical Laboratory. The first chemical compound of plutonium, free from carrier material and all other foreign matter, was prepared on 18 August 1942. This historic day marks man's first sight of the element plutonium and, in fact, the

first sight of a synthetically produced isotope of any element. The first weighing of a pure compound of plutonium occurred on 10 September 1942, when 2.77 micrograms of the oxide (PuO_2) were weighed. Thus, we are also commemorating the 20th anniversary of the first isolation and the first weighing of the element plutonium.

The Bismuth Phosphate Process continued in operation at the Hanford Engineer Works for a number of years, certainly a monument to the investigational methods of radiochemistry and ultramicrochemistry. This process was eventually replaced by solvent extraction processes.

It is not possible in this short account to go on to describe the potential peacetime role of plutonium in the field of civilian nuclear power, and as a source of power in other special applications. Plutonium has a great future, capable of much development in these areas. It is also beyond the scope of this discussion to describe the discovery of and the related early work on other transuranium elements and the relationship of this work to that on plutonium. These elements all have an intimate, familial relationship to plutonium, and a description of this relationship would also present an interesting story.