

Products of Neutron Irradiation

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I will describe some of my research on products of the neutron irradiation of uranium. Most of the work was conducted in Berkeley during the period 1936–1940 at Lawrence's Radiation Laboratory. The research I will discuss included the first American discovery of fission products and the chemical isolation of element 93.

In the nearly 50 years that have ensued since the discovery of fission, many investigators have examined the half-lives and other characteristics of the products. Since the precise data are already part of the permanent literature, I will not present a detailed description of my research findings. Rather, I will portray my activities as a lowly graduate student in what was then the world's leading nuclear physics laboratory.

Prior to joining the Radiation Laboratory in August 1935, I obtained a bachelor's degree in chemistry and a master's degree in physics at Washington State University. On arrival in Berkeley I immediately proceeded to the Laboratory. Ernest Lawrence was there and without delay directed me to paint the cyclotron magnet. The vacuum chamber of the cyclotron was being repaired. The 80-ton magnet was black, and he wanted it painted a battleship gray. I went about the business and was soon joined by Lawrence himself. During the ensuing days, I was asked to do some odd jobs but soon was assigned to heavy duty as part of the cyclotron crew. At that time, the machine was scheduled to be operated continuously from 8 a.m. to 11 p.m. seven days a week. One main use of the beam was to irradiate elements directly or with neutrons to produce new artificial radioactivities. A second objective was to produce radioactive isotopes such as ^{32}P for use in tracer experiments elsewhere. In addition, Lawrence was constantly pushing to increase the beam current or voltage.

The cyclotron operating schedule was divided into three shifts: roughly 8 a.m. to 1 p.m., 1 p.m. to 6 p.m., and 6 p.m. to 11 p.m. But that was only nominal, because often leaks developed, or there were requirements to change an internal filament used to ionize deuterium, or to take the vacuum chamber apart. When such emergencies arose, all hands were supposed to respond. In 1935 and 1936, I was one of the few graduate students in the Lab. Most of the members were postdocs. They were assigned three shifts a week. I was assigned six, plus emergency duty. Emergencies were frequent, because the cyclotron chamber had joints that were sealed with beeswax and rosin, or with a plastic liquid called Glyptal. To function properly, the chamber vacuum needed to be of the order of 10^{-6} mm. Thus a tiny leak made the machine inoperable. We hunted for leaks by exposing suspected regions to the methane of natural gas. This molecule went through the leak faster than air and produced a change in the level of the vacuum observable at the control panel.

In addition to the leaks or equipment failures that occurred during normal operations, the cyclotron crew had to contend with the enthusiasm of Lawrence. From time to time he would take over as operator of the cyclotron. Up to a point he was skillful in achieving maximum performance. However, he often pushed the variables, such as the filament current involved in forming the deuterons, to such an extent

that a breakdown occurred. The required repairs often occupied 24 to 48 hours.

For the first two years of my time at Berkeley, I spent an average of 40 hours a week on what amounted to menial care of the cyclotron. I was, of course, expected to do other things. As a teaching assistant, I was a lab instructor, and I corrected blue books of examinations taken by classes of 500 elementary physics students. Correcting blue books for Leonard Loeb was a trying adventure. He took the view that students should be given partial credit on a question if they showed some sign of understanding what the problem was all about. In some instances the 500 students would devise about 50 different ways of not getting the right answer to a question. Apportioning partial credit to the various versions would have taxed Solomon. Even more trying was maintaining consistency, which was necessary because the students compared answers and grades.

Graduate students were required to take graduate courses and ultimately to take prelims to prove they had mastered them. This part of graduate school was something of a torture for me. None of the professors of the courses were good teachers, and none seemed enthusiastic about meeting their classes. Nor did they exhibit judgment of what was interesting or important. I learned little and barely squeaked through the prelims.

One day in early 1946, Lawrence remarked about a paper by Fermi and colleagues in which they reported that they had irradiated uranium with neutrons and had produced beta emitters that they believed were transuranic elements. In the natural uranium, thorium and related decay series electron emission is followed by emission of alpha particles. The high levels of neutrons available from the cyclotron made it seem possible that irradiation of uranium might lead to detectable alpha particles emitted by the new transuramics. I irradiated some uranium and separated "transuramics" following the procedures described by Fermi. Lawrence and I jointly looked for alpha particles, but found none. My efforts to discover more about the effects of irradiating uranium with neutrons did not stop there. However, the more intense irradiation yielded only more complexity. When a single radioactive isotope is produced, it decays exponentially with a characteristic half-life. When the intensity is plotted as a function of time on semilog paper, the result is a straight line. If two isotopes of substantially different half-life are present, the decay of radiation can be resolved into the components, provided the decay is followed for a sufficiently long time. In the period 1936–1938, I made innumerable neutron irradiations of uranium and isolated products that precipitated as sulfides and were supposedly ekarhenium or its daughters. Depending on the length of irradiation, I observed a different decay rate of the radiation. But when plotted on semilog paper, the result was a continuous curve. This indicated that a complex mixture of decay products had been formed. I became dubious of the half-lives reported by the Fermi group, but, since I had no unique answer, I said nothing. For a time I relegated the uranium question to a lower priority and turned to such matters as passing prelims.

By 1937 my standing in the hierarchy of the Radiation Lab

had improved. One day Donald Cooksey approached me asking my help to find the leaks in a newly designed cyclotron vacuum chamber. This one had an enlarged diameter of 37 in. It would make possible the production of 8-meV deuterons. Best of all, it would not use beeswax and rosin. Instead, much of the assemblage would be welded together, and, where necessary, rubber gaskets would be employed. Cooksey had assembled the chamber and had attempted to obtain a good vacuum in it. He had failed, and he concluded that some of the welds were leaking. Ultimately, I found the leaks. There were 23 of them of varying sizes. The situation was one in which it was only feasible to find the largest leak first, stop it, and then proceed to find the next largest. When the whole deed was done and the new chamber was installed, the cyclotron produced the more energetic beams, and the operation of a chamber devoid of beeswax was more trouble-free.

By the summer of 1937, demand for tracers from the cyclotron had increased substantially. Operation of the machine was scheduled on a 24-hour basis. I spent many a lonely night on the owl shift, which went from 11 p.m. to 8 a.m. My memory is that I was an excellent operator who made the necessary adjustments to keep the beam constantly at maximum and that there were no breakdowns while I was in charge.

By early 1938 I had completed the required courses and finished most of the prelims. I had been given a research assistantship. The cyclotron was operating more reliably. Thus I had more freedom to resume research. At that time, each member of the laboratory had to make his own measuring instruments. With some help from others I became equipped with a sensitive electroscope and a Geiger counter. I made my own Geiger tubes, determining their proper operating voltages. I also built an ionization chamber that could be filled with methyl bromide to increase its sensitivity to X-rays. Later I made a bent-crystal X-ray spectrometer. Thus I had the wherewithal to pursue independent research. What to do? There was only limited inspiration or guidance to be had. Lawrence's top interest and priority by far was designing and financing machines that could produce higher energy particles. The one person in the Lab who was enthusiastically creative and who had time for a graduate student was Luis Alvarez. We frequently went to the Student Union nearby to have coffee. I sought his advice, and he encouraged me to resume work on the neutron irradiation of uranium. I did so and isolated a 3-day radioactivity that had a 2.4-hour daughter. The chemistry used to separate the 3-day activity was one that an eka-rhenium element might have.

About that time, Alvarez discovered that electron capture occurred in the decay of ^{67}Ga , leading to emission of characteristic X-rays. In addition, such X-rays were produced as a result of internal conversion of energy that was also emitted as gamma rays. I looked for X-rays from the combined 3-day parent-daughter and found them and gamma rays present. However, steeped in the Fermi approach to transuranics, I attributed the radiation to possible L X-rays of a transuranic element. Accordingly I set out to find a method for measuring their wavelength. Alvarez was aware of a fairly recent publication about a sensitive bent-crystal X-ray spectrometer, which I proceeded to build and test. I obtained a rock-salt crystal with dimensions $5 \times 2.5 \text{ cm} \times 2.5 \text{ cm}$. With a razor blade, the crystal was readily cleaved to form a rectangular plate 3 mm thick. When immersed in a saturated solution, the plate was easily bent in a jig to have a radius of curvature of 30 cm. The concave surface was later machined to a radius of curvature of 15 cm. X-rays from a source placed on a 30-cm circle were focused by the crystal to converge on the circle at a point opposite to the source. Fluorescent X-rays of various elements generated by exposure to a conventional X-ray tube were used to provide calibration lines. X-ray film was used as the detector. I used the X-ray spectrometer to identify characteristic X-rays as-

sociated with the decay of ^{64}Cu , ^{67}Ga , ^{80}Br , and a technetium isotope (*Phys. Rev.* 1939, 56, 753–757). I was prepared to tackle the X-ray emitter associated with the product of neutron irradiation of uranium. Intensity of the radiation was the limiting factor. Experience with the other X-ray emitters informed me that I must irradiate a large amount of uranium with a long-duration exposure to as many neutrons as possible.

But at that time the financial position of the Radiation Lab was precarious, and I could not expect the Lab to buy the necessary chemicals. For Christmas, 1938, my parents sent me \$25 to buy a new suit. In early January 1939, my wife and I started to San Francisco to do the shopping. On the way there, we encountered Braun, Knecht and Heiman, Chemical Suppliers. We emerged from their shop with 10 pounds of yellow cake, a crude uranium compound. I found it to be very impure. Among other things, it contained silicates that formed gels when the product was acidified. It was only after some effort that the uranium was freed of major impurities.

In late January I made an intense, prolonged irradiation of uranium, isolated the 3-day activity in a tiny amount of precipitate, and placed it on my X-ray spectrometer. On January 27, before the exposure was complete, Luis Alvarez burst into the Radiation Lab with the news that the *San Francisco Chronicle* contained a story about the discovery of uranium fission. At that moment I was operating the cyclotron. The news left me stunned. For a whole day I was intellectually paralyzed. The next morning I hastened to my laboratory and proceeded to identify the X-ray by use of critical absorption measurements. I then identified the 2.4-hour activity as an iodine isotope. On about February 1 a short letter was sent to the *Physical Review*. It was received February 3 and published in the February 15 issue.

As of February 1, 1939, the possible scope of products of uranium fission was uncertain. There was an outside chance that half of the periodic table might be involved. Through the kindness of Willard Libby, I obtained samples of virtually all the elements and made solutions of them. I spent a few days in concentrated study of an advanced text of qualitative chemical analysis. I then made some group separations that convinced me that many elements in the middle of the periodic table were fission products, but that elements of low and high atomic number were not involved. The decay curves were complex, and I concluded that I had better concentrate on elements in the vicinity of tellurium. The decision to do so was influenced by the existence of good procedures for separating those elements and the fact that the isolations could be performed rapidly. For example, antimony can be volatilized as stibine (SbH_3), and subsequent passage of the gas into silver nitrate solution yields a precipitate of Ag_3Sb . In one experiment it was possible to begin measuring radioactivity of the sample four minutes after cessation of neutron irradiation. The only other element capable of being volatilized in the procedure was germanium, which was shown to have negligible radioactivity. Good fast procedures were also employed to isolate tellurium and iodine activities. Tellurium was precipitated from a 3 N hydrochloric acid solution by passing in sulfur dioxide. Other elements that are reduced simultaneously include gold and selenium. They were separately shown to be of negligible activity.

During the next two months I moved rapidly to identify three antimony, seven tellurium, and four iodine products of uranium fission. The results were included in *Letters to the Physical Review* and then incorporated in an article in the *Physical Review* published July 1 as the lead article in Vol. 56. In April, I defended my thesis based on the fission work and was formally awarded the PhD degree at commencement on May 8.

Nearly 50 years later, I can take pride in the contents of the article. The chemical separations were well-designed,

reliable, and quickly performed. A large series of experiments was performed that established parent-daughter relationships. At the time, these results are the most complete determinations of decay chains of any group of uranium fission products. For example, the tellurium activities identified included entities with half-lives of 25 min, 43 min, 60 min, and 70 min, 10 h, 30 h, and 77 h. Small wonder that a composite mixture of such a group and their decay products would yield an undecipherable curve. However, by a variety of approaches, including observation of formation of some of the isotopes from antimony and repeated observations of growth of specific iodine activities from tellurium, it was possible to discover the various tellurium isotopes.

After my paper on fission products appeared July 1, I was approached by Harvard, Washington University at St. Louis, and the Carnegie Institution of Washington (CIW). Vannevar Bush, President of CIW, had authorized Merle Tuve to build a 60-inch cyclotron. Tuve had dispatched Richard B. Roberts to Berkeley to become well-informed about the proposed 60-inch instrument. I had several conversations with Roberts and was favorably impressed with his intelligence and humanity. I had been aware of some excellent work on proton scattering that Tuve and Hafstad had performed in about 1936. The Department of Terrestrial Magnetism (DTM) had an excellent reputation among physicists. Thus when I was offered a position at DTM to help build a cyclotron and later to be active in its applications, I accepted the position.

The move to Washington, DC, ended studies of uranium fission, but I retained an interest in a particular product of neutron irradiation.

When uranium is irradiated with neutrons, fission products are created, but in addition a 23-minute beta-emitting isotope of uranium is formed. This radioactivity had been observed well ahead of the discovery of fission. It was inferred that decay of the isotope gave rise to a transuranic element, number 93. While others were making experiments involving neutron irradiation of uranium, McMillan had conducted studies of thin films of uranium compounds. He found that the highly energetic fission products left the film and could be captured. However, the 23-minute uranium cavity remained in the thin film. In addition, he noted that a 2.3-day beta emitter was also present in the film. McMillan attempted to get more chemical information about the 2.3-day activity. Later, Segre investigated it. He noted that the substance behaved like a rare earth. He proved that it was not actinium, thorium, or protoactinium and that it did not behave like rhenium, which is the element below element 93 in the periodic table. By observing the decay of the 23-minute uranium over many half-lives, he hoped to establish a possible genetic relationship between the 23-minute and 2.3-day activities, but was unsuccessful. His letter was published in the *Physical Review* in June 1939.

In January 1940 I reread the Segre letter and was immediately of the strong opinion that the 2.3-day activity was that of a transuranic element. I knew that cerium could exist in valence states 3 and 4. I also knew that Jesse Beams had developed a very high speed centrifuge that could separate

isotopes. A comparison of the mobility of one of the known heavy rare earths with that of the 2.3-day activity might produce important evidence.

I approached Tuve with these thoughts and found him interested. However, he was concerned that, if I were to conduct chemical operations on the DTM premises, the background count due to alpha particles might be raised. He arranged lab space at what is now American University in a room with Sterling Hendricks. Tuve also obtained platinum dishes from the Geophysical Laboratory enabling me to conduct fluoride precipitations in acid solution. Lawrence Hafstad conducted some neutron irradiations for me using the Van de Graaf generator, which was then operating at only about 2 meV and a few microamperes. The compound irradiated was uranyl nitrate. The two irradiations and subsequent chemistry produced disappointment. The amount of radioactivity was very small in comparison to what I had known in Berkeley, and results of the chemical separations were inconsistent. I concluded that if I were to make further progress, I must have the intensities available at Berkeley.

When I arrived there in mid-May, I found that McMillan was still interested in the 2.3-day activity, and he quickly agreed to irradiate another thin film of $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and to arrange chemicals, platinum ware, and laboratory space for me. Within a day after my arrival at Berkeley, I conducted the crucial experiment. In the presence of a strong oxidizing agent (bromate), the activity did not precipitate with cerium in acid containing fluoride. When the solution was made reducing and more cerium was added, the precipitate contained the 2.3-day activity. On the basis of this knowledge, it was possible to conduct confirmatory experiments in which large amounts of uranium were irradiated and the 2.3-day activity was isolated free of fission products. This permitted exploration of other chemical properties of the substance. It became clear that element 93 represented one of a new series of rare earths, and this was confirmed and extended by later creation of higher transuranic elements. For example, element 93 behaved like thorium when in the reduced state and like uranyl uranium when in the oxidized state. That is, thorium iodate is insoluble, as is the corresponding iodate of neptunium. Sodium uranyl acetate is insoluble, as is neptunium in the oxidized state when sodium acetate is present. It was possible to prove a genetic relationship between the 23-minute and the 2.3-day activities. For this experiment activated uranium was twice quickly purified by precipitation as sodium uranyl acetate. The precipitate was dissolved in HF and the solution saturated with SO_2 . Then equal quantities of a cerium salt were added at 20-minute intervals and the precipitates filtered out. It was possible to follow the decay of the 23-minute uranium over nine half-lives and to observe the corresponding production of the 2.3-day element 93. In total, I spent five days in Berkeley in May 1940, part of which was devoted to writing up the letter that appeared in a June 1940 issue of the *Physical Review*.

Those were five exciting and gratifying days in May 1940, but for me their drama was shadowed by worrisome events simultaneously occurring in Europe. The mighty German war machine was overrunning France.