Madame Marie Curie – Radioactivity and Atomic Energy*

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As late as 1895 physicists and chemists seemed to be convinced that the ultimate particles of matter consist of atoms which cannot be further broken down. In 1896, a new phenomenon, i.e., radioactivity, was discovered by Henri Becquerel (1852-1908) of France, which changed our ideas regarding the ultimate particles of matter. The discovery of X-rays by Prof. Roentgen (1845-1923) in 1895, of cathode rays by J. Plucker (1801-1868) and others also helped in modifying the scientists' notion regarding the atom.

Prof. Becquerel was the Head of the Physics Department of the Natural History Museum in Paris and was an authority on fluorescence of uranium compounds. He exposed a fluorescent potassium uranyl sulphate crystal to sunlight and then placed it on a photographic plate wrapped in black paper and observed an image of the crystal on the photographic plate when it was developed. In the next few days there was no sunlight in Paris and Becquerel put the crystal over a photographic plate wrapped in black paper. In this case also an image of the crystal appeared on the plate. He reported to the French Academy of Sciences in February 1893 (Compt. rend. 122, 420; 24 February, 1896) that this salt, 'must emit radiations which are capable of passing through paper, opaque to ordinary light'. He also observed that the same effect was produced in the dark and by other uranium compounds, and the radiations given out by uranium made a gas conduct X-rays and cathode rays. This was the discovery of the radioactivity of uranium, which is spontaneous decomposition of matter into smaller particles. This subject of radioactivity was greatly advanced by Madame Curie with the help of her husband, Pierre Curie, because they made the capital discovery that a very highly radioactive material, which was named radium, was present in the mineral pitchblende even after the removal of uranium compounds. Radium decomposes spontaneously and much more vigorously with liberation of heat and other radiations than the uranium compounds. This discovery made it possible for man to visualise the production of energy by the breaking of atoms.

Marya (Marie) Curie was the daughter of a Polish Professor Sklodovska and was born at Warsaw on November 7, 1867. As Poland was backward in science at that time, she had to learn science from books; but, in 1890 she could carry on some elementary experiments in physics and chemistry in her cousin's laboratory. She wanted to study science in the Great Centre of

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Learning, Paris, and had to save money for this purpose by serving as a governess for about six years. She joined for a short while her sister and brother-in-law at Paris. Soon afterwards she shifted to cheap lodgings and registered herself for Licence Degree in Science Faculty, University of Paris, Sorbonne, in 1891. She obtained first position in Licence in Physics in 1893 and second position in mathematics in 1894 whilst living in Paris under great privations. In 1893 she carried on some research work on the magnetic properties of steel under Prof. G. Lippmann, a Nobel Laureate in Physics and came in contact with Prof. Pierre Curie of the *Ecole de Physique et de Chimie*, Paris, a great authority on magnetism.

From 1896 she carried on the chemical analysis of numerous uranium minerals found in Prof. Becquerel's Institute and other laboratories in Paris and made a striking observation that the uranium content of these minerals and their power to discharge a charged gold leaf electroscope do not go hand in hand. The power to discharge a gold leaf electroscope, which is caused by the radioactivity of the minerals and the ionisation of the surrounding air, may be large, specially of pitchblende, even after the separation of uranium. By that time, i.e. in 1895, she was married to Prof. Curie who realised the importance of the investigations undertaken by his wife and joined her in these researches. The husband tackled this problem from the physicist's point of view and concentrated on the determination of the properties of the radiations given out. He and others proved that the radiations emitted by radioactive bodies consist of a α-particles, positively charged, consisting of helium, β-rays which are negatively charged and γ-rays, similar to x-rays, are given out. Madame Curie devoted herself to the chemical manipulation of separating large amounts of extraneous substances dealing with one ton of pitchblende supplied by the Austrian Government from which uranium was separated. In April 1898 she came to the conclusion that pitchblende contains an unknown element, much more radioactive than uranium. The problem was to separate the active material from pitchblende by chemical group separation and fractional crystallisation. The radioactivity of the products was determined by the electrometer method. The laborious and the tedious chemical separation was undertaken by Madame Curie. One evening after returning to their laboratory in the *Ecole de Physique et de Chimie*, the Curies were pleasantly surprised to find that their radioactive products were emitting light in the dark room.

Discovery of Radium by Pierre and Madame Curie

In June, 1898 a radioactive element was obtained in bismuth sulphide precipitate and was named polonium after the name of the motherland of Madame Curie. In December, 1898 the discovery of radium in the barium sulphate precipitate was announced. This impure radium preparation showed a radioactivity which was million times greater than that of uranium.

A third radioactive element was discovered in the ammonium hydroxide precipitate containing ferric and rare earths compounds by A. Debierne in 1900, who was helping Pierre and Madame Curie. They called this product actinium, which was also independently discovered by O. Giesel (1852-1927), who was a chemist in a quinine factory in Brunswick. It has been reported that Giesel also prepared and sold radium bromide and his own breath was found to be radioactive, although he lived over 25 years after the discovery of actinium. Madame Curie presented her thesis for the D.Sc. degree in the Sorbonne in 1902 embodying her researches on radium and radioactivity, and the same was published in the following year. In 1902 she determined the atomic weight of radium by precipitating 0.09 of radium chloride with silver nitrate and obtained a value of 225 as the atomic weight of radium. Again, in 1907, working with 0.4 of radium chloride, she found the atomic weight to be 226.4 taking silver as 107.88 and chlorine 35.46. The eminent authority on determination of atomic weight, Prof. Honiogschmid of Vienne, in 1911, obtained a value of 225.95. Aston's mass spectograph indicated the value as 226.1. The accepted value today is 226.05. In 1910 Madame Curie and Debierne isolated metallic radium by electrolysing a solution of radium chloride with a mercury cathode. The mercury was separated from the amalgam by distillation.

Radioactivity was intensely studied all over the world, specially by Rutherford (1871-1937) in Canada and England, Soddy (1877-1956), Fajan, Boltiwood, O. Hahn and others. Rutherford studied the activity of uranium and thorium and reported in 1899, that the rays emitted by uranium were of two kinds (i) those stopped by thin sheets of aluminium which he called α-rays, and (ii) the other requiring much thicker sheets of aluminium designated as β-rays, which are deflected by a magnetic field.

Madame and Pierre Curie reported in 1900 that β-rays carry a negative charge. Becquerel, in 1900, by deflection in electric and magnetic fields determined the velocity (1.6×10 cm. per second) and the ratio of charge to mass ($e/m = 3 \times 10^{17}$ e.s.u./g of β-rays). These values are of the same order of magnitude as those for cathode rays. Strutt (4th Baron Rayleigh) in 1901 and Crookes in 1902 suggested that α-rays were positively charged particles of relatively large mass. This was confirmed by Rutherford in 1903. Villard discovered the rays which were called γ-rays by Rutherford. They are more penetrating than β-rays and are not deflected by magnetic field.

In 1910 Madame Curie could prepare one gram of radium from pitchblende after great efforts and presented this valuable material to her laboratory. In 1920 she was invited by the women of America and many honorary degrees and distinctions were showered upon her, and the women of America subscribed for the purchase of another gram of radium for her institute.

Madame Curie, First Woman Professor of the Sorbonne and twice Recipient of the Nobel Prize

In 1903 the Davy Medal of the Royal Society of London was awarded to Professor Pierre and Madame Curie. The Nobel Prize of 1902 in Physics was first awarded to Prof. Becquerel and Pierre Curie, who represented to the Nobel Committee that the discovery of radium was as much due to him as to Madame Curie, and, the Committee agreed to award half of the Nobel Prize to the husband and the other half to the wife. In April, 1906 Pierre Curie was killed in a street accident in Paris. The authorities of the University of Paris appointed Madame Curie as Pierre Curie's successor to the Chair of General Physics at the Sorbonne. This was the first time that a woman was appointed as University Professor. In 1911 Madame Curie was awarded the Nobel Prize in Chemistry. Thus she was the only recipient of the Nobel Prize twice in science.

Since 1900 the physiological effect of radium rays was investigated by the Pasteur Institute of Paris and the Paris University jointly established a radium institute known as Pavillon Curie with Madame Curie as the Director of Physical Sciences, which was ready for occupation in July 1914-1918. Madame Curie installed X-ray equipment for military purposes in 20 motor cars and 200 hospitals in different parts of France for the trreatment of the wounded.

From her research institute 483 scientific communications of which 34 were theses and 31 publications in the name of Madame Curie appeared during the period 1919 to 1934. Doctor Reguad, Director of the Biology and Medicine Branch of the Pavillon Curie treated 8,319 patients from 1919 to 1935. Baron de Rothschild and Lazard Freres and an annonymous donor contributed 3.5 million francs to the Curie Foundation.

Life Pension Sactioned by French Government in 1923

On December 26, 1923, i.e., 25 years after the discovery of radium, the French Government voted 40,000 francs as annual pension to Madame Curie with the right of inheritance to her daughters Irene and Eve.

Prof. Regaud wrote: 'Madame Curie can be counted among the eventual victims of the radioactive body which she and her husband discovered'.

Death of Madame Curie caused by Radioactive Emanations

In 1934 she became seriously ill and proceeded to the Sancellemoz Sanatorium where she died. The Officer-in-Charge, Doctor Tobe recorded: 'The disease was a plastic pernicious anaemia of rapid, feverish development. The bone marrow did not react, probably beacuse it had been injured by a long accumulation of radiation'. Due to constant exposure to the highly toxic rays from radioactive substances investigated by them, Irene and her husband also died prematurely.

Madame Curie – a brilliant Director and Lecutrer

Prof. Einstein stated: 'Marya Curie is of all the celebrated beings the only one whom fame has not corrupted'.

I had the honour of working in her institute for two years – 1917-1919, and I found that she took great pains in preparing university lectures with experimental demonstrations in which her daughter Irene helped her. After receiving the Nobel Prize with her husband, Prof. Curie Joliot, Irene visited different countries and visited India in 1950.

Prof. Jean Perrin, the Nobel Laureate, who was also my teacher, frequently stated: 'Madame Curie is not only a famous physicist, she is the greatest laboratory director I have ever known'. During this period a galaxy of brilliant mathematicians and scientists, Henri Poincare, Appel, Painleve, Le Chatelier, Bouty, Lippmann, Haller, Behal, G. Bertrans, Roux, Delepine, Caullery, Urabain, Langevin, Duclaux, Job, Matignon, Jungfleisch, Pierre and Madame Curie, Mouton, Fabry, D. Berthelot, Moureu, Dufraisse, Grignard, Fournier and others were teaching in Paris.

ATOMIC DISINTEGRATION

The collision of fast α-particles, protons, deuterons or neutrons with atoms of other elements may cause the breaking of the nucleus. Rutherford reported in 1919 and 1920 that nitrogen exposed α-particles emit long range protons which came from the nitrogen nucleus. Similarly, Rutherford and Chadwick in 1921, Blackett in 1922 and Harkins and Ryan in 1923 demonstrated the disintegration of atoms by the cloud chamber method. When α-particles having mass 4 and charge 2 bombard nitrogen atom, mass 14 and nuclear charge 7, they enter the nucleus producing a particle of mass 18 and nuclear charge 9, which is an isotope of fluorine. This nucleus emits a proton, mass 1 and charge 1, producing a nucleus of mass 17 and charge 8, which is an isotope of oxygen. In 1932, Cockroft and Walton disintegrated lithium into helium. This was the first artificial atomic disintegration by bombardment with high energy protons from hydrogen ionised in a discharge tube and accelerated by high potential difference. In 1933, F. Joliot and Irene Curie observed that both positive and negative electrons are emitted by thin layers of berylium, boron and aluminium bombarded by particles from polonium. In 1934, they reported that the emission of positron persisted even after the removal of the source of α-particles. This was the first discovery of artificial radioactivity.

Fission of Uranium to Barium by Otto Malhn and Influence of Chemical Evidence in Fission

E. Fermi and collaborators, by bombarding uranium, atomic number 92, with slow neutrons obtained by passing through water or paraffin wax, thought that they had obtained an element of atomic number 93. They reported similar results with thorium in 1934, but Frau Ida Noddack criticised Fermi's chemical evidence and stated: 'It

is conceivable that in the bombardment of heavy nuclei with neutrons, these nuclei break up into several large fragments which are actually isotopes of known elements, not neighbours of irradiated elements'. O. Hahn and Strassmann in 1938, by co-precipitating the solution of the product of the bombardment of uranium with neutrons with a barium salt solution, thought that they had obtained an isotope of radium. After β-ray decay, the products of the bombarded material were precipitated with lanthanum. Hence, the authors regarded them as the actinium isotopes. Madame Joliot Curie and Savitch, in 1937, reported that the bombarded product concentrated with lanthanum rather than with actinium.

Early in 1939, Hahn and Strassmann concluded that their supposed radium was actually barium, and from chemical evidence they concluded that their actinium and thorium were really lanthanum and cerium. The authors stated that their experimental results contradicted the accepted views in nuclear physics. Lise Meitner, who was a collaborator of Prof. Hahn for a number of years in Berlin, and O.R. Frisch, in 1939, reported that nuclear physics must give way to chemistry and stated: 'On the basis of present ideas about the behaviour of heavy nuclei, an entirely different and essentially classical picture of these new disintegration processes suggests itself. It seems possible that the uranium nucleus has only small stability of form and may, after neutron capture, divide itself into two nuclei of roughly equal size.

It was soon discovered that the fission of uranium by neutrons liberates a large amount of energy according to Einstein equation: $E = Mc^2$ where E = energy liberated; M = mass destroyed and c = the volocity of light. Both isotopes of uranium U_{235} and U_{238}, are split by fast neutrons but U_{235} is broken up by slow neutrons. In this process, more neutrons are liberated, but the fast neutrons escape quickly and it is only the slow neutrons which are effective for breaking U_{235} and the creation of an atomic bomb.

Discovery of Transuranium Elements

In modern times increased neutron fluxes are being achieved as nuclear reactors are improving and 12 new elements beyond uranium have been isolated. The first four of these transuranium (94), americium (95) and curium (94), americium (95) and curium (96) can be manufactured in kilograms whilst californium (98) in grams. The chemistry of berkelium (97) has been studied with submicrogram amount and, hence, this element along with einsteinium (99), fermium (100), has only been obtained in traces. The elements upto fermium (100) are formed from U_{238} by succession of neutron capture and β-ray decay as shown by the reaction leading to the discovery of neptunium and plutonium.

It has been found that elements of atomic number of 100 or more decay by spontaneous fission with very short half life, so that their preparation cannot be achieved by exposing uranium or transuranium elements to a reactor or

more rapidly by exploding a thermo-nuclear device in a suitably sealed underground cave and processing the debris. Such elements are prepared by bombarding plutonium, curium or californium with boron, carbon, nitrogen, oxygen or neon ions accelerated in a cyclotron or linear accelerator. The yields of mendelevium (101), nobelium (102), lawrencium (103) and element 104 are extremely small. Along with transuranium elements, fair amounts of technetium (43) and promethium (61) are formed as fission products in nuclear reactors. Polonium 210 and actinium 227 can be readily synthesised by neutron irradiation of bismuth and radium respectively.

Atomic Fission Markedly Increases Production of Highly Dangerous Radioactive Materials

Before the fission of uranium by neutron in 1939, the amount of radioactive matter in use in the hospitals and laboratories throughout the world was only equivalent to a few hundred grams of radium of atomic weight 226. Today, a low power (10 megawatt) nuclear reactor fed with natural uranium will produce fission products giving out α-radiations equivalent to one ton of radium together with α-particles emitting transuranium elements equivalent in activity to 200 grams of radium. The generation of large amount of radioactivity is highly hazardous and the investigations of the chemical properties of the new elements are not straightforward because of their radioactivity, which is more intense for the higher elements. The radiations emitted have two important consequences relating to health hazard and to their chemistry. The first is that they are among the most toxic substances known to man because of the irreversible damage to tissue caused by such materials. When ingested, they are selectively retained in critical organs in the body. Plutonium, for example, tends to concentrate in the bone; other elements in the series are retained in the kidneys or in the gastrointestinal tract. The high toxicity becomes immediately apparent when one compares the maximum permissible concentrations per cubic metre in air for continuous exposure, assuming a 40-hour week with those for the more conventional poisons. The figures for carbon monoxide and hydrocyanic acid are 100 mg and 10 mg respectively while those for ^{239}Pu and ^{241}Am are 3.1×10^{-8} mg and 1.8×10^{-9} mg respectively many orders of magnitude smaller than those for hydrocyanic acid.

Chemistry played a major part in the discovery of fission process by identifying barium as one of the products of thermal-neutron bombardment of uranium. Chemical processes have also played an essential role in the application of the fission process to the production of nuclear power. These processes involve the treatment of several thousand tons of uranium per annum; this tonnage is comparable to that of the metals, mercury and silver, substantially lower than elements such as arsenic, tin and nickel, yet rather larger than gold, beryllium and tantalum.

Two sequences of chemical processes are involved. In the first, ore concentrates

(largely U_8O_3) are converted to nuclear fuels, uranium metal or dioxide. In the second, the nuclear fuels, after removal from reactors, are treated for the recovery of useful constitutents, such as plutonium or fission-product strontium. The radioactivity in the first category is relatively low, but in the second very high.

Thorium as Fissionable Material

Since the application of uranium in atomic fission as a power source has been developed to such an extent, attention has been directed to thorium which is more abundant in nature than uranium, as a possible source of the secondary nuclear fuel U^{233}. According to J. Paone (1960) an important potential use of thorium is its application in the field of nuclear energy. By the capture of slow neutrons Th^{232} is converted to Th^{233} a negative beta particle being emitted with a 23-minute half life. The product of Th^{232} is protoactinium, which is also beta active with a half life of 27.4 days. It decays into fissionable U_{233} and a long lived α -particle with 1.63×10^5 years half life. Thus, the thorium nucleide, upon bombardment by thermal or slow neutrons, becomes eventually a potential nuclear fuel material capable of initiating a chain reaction. Nuclear reactions employing a blanket of thorium around the reactor are capable under certain conditions of producing as much and possibly more fuel than is consumed in fission. A number of major reaction projects proposing to use thorium have been under way for several years in the USA.

Atomic Energy not yet in the Picture of World Energy Resources

The discovery of the neutron fission of uranium to barium and opther elements in 1939 by Prof. Otto Hahn with liberation of tremendous energy has led to fabulous activity and expenditure all over the world for obtaining atomic energy for the use of man. But, uranium occurs on the earth's surface to the extent of 4 grams per ton of the earth's crust, whilst thorium, another fissionable element, is three times more abundant. Moreover, 0.7 per cent of natural uranium is uranium 235 which actually breaks up in energy production. Although, 12 new transuranium elements have been synthesised in the last 26 years, the consensus of expert opinion seems to be that even on the basis of the most optimistic assumption about the future rate of nuclear developments, the contribution of atomic power until 1975 to growing energy demands will be marginal. (*The Petroleum Handbook*, 4th edition, London, 1959, page 20).

'Nuclear power offers no panacea for the world's energy problems. The adoption of fission power will be slow and its rate will depend ultimately on the exhaustion of fossil fuel reserves. Fusion power, while potentially having many advantages over fission power including an inexhaustible fuel supply for negligible cost, has not yet been established as feasible and its costs cannot be reliably assessed. Both types of nuclear power are uniquely adapted to the generation of electrical power and less so to the production of other forms of energy, such as those now used in

comfort and process heating or in land transportation. Thus, a radical change in existing energy consumption patterns is required before the fossil fuels are finally enhausted.' (Robert C. Axtmann, pp. 488-495 in *The Population Crisis and the Use of World Resources*, edited S. Mudd, 1964, The Hague, Dr W. Junk, Publishers).

Beginning of Atom Bomb

After the beginning of the Second World War in 1939, Prof. Otto Hahn of Berlin approached Hitler and informed him that he was in a position to manufacture a powerful bomb from his discovery of atomic fission. Hitler asked him how much time he would take for this purpose and Hahn replied that it would take two years. But, Hitler was impatient and he stated that he had no use for a discovery which cannot prolduce tangible result within six months.

On the other hand, after the occupation of Denmark by Hitler, Neils Bohr, the great Danish atomic physicist had to leave his own country for USA as he was a Jew. But, before he left Denmark, he discussed the details of atomic fission with Lise Mertner who was associated with Hahn in atomic fission studies and who being a Jewess was on her way to Sweden from Berlin. After reaching USA, Bohr contacted A. Einstein, who also was of Jewish origin and a Professor in the Princeton University as a nautralised American citizen. These two great men discussed the fabrication of the atomic bomb and Einstein wrote to President Roosevelt to take up this work. Roosevelt consulted Churchill, the Premier of the United Kingdom, who was encouraged by Lord Cherwell (Prof. Lindemann), Churchill's scientific adviser. Also, Churchill sent some of his able atomic pysicists, mathematicians and engineers to join the USA experts. This tremendous undertaking, which was extremely difficult in execution, resulted in the construction of atomic bombs under the leadership of R. Oppenheimer, another Jew from Germany and settled in the USA. Under the Presidentship of Truman, the two bombs fell on Hiroshima and Nagasaki in 1945, and, thus, began the atomic age with all its complications and dangers.