Marie Skłodowska-Curie – on the shoulders of giants, thinking outside the box*

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Introduction

Hundred years ago, in 1913, the first Polish Radiological Laboratory was opened in Warsaw under the auspices of the Warsaw Scientific Society. In spite of the distance between this city and Paris, the scientific supervision on the Laboratory [1] was entrusted to Marie Skłodowska-Curie (1867–1934), the honorary member of the Society, professor of the Sorbonne, organizer and head of the Curie Laboratory at the Radium Institute in Paris, a co-laureate of the 1903 Nobel Prize for Physics [2] and the winner of the 1911 Nobel Prize for Chemistry [3] – admired worldwide for the discovery of the cancer-curing radium. Reciprocating the reverence of her hosts, Marie Skłodowska-Curie publically expressed her gratitude to Polish scientists who more than 20 years earlier had taught her analytical chemistry so well that she was able to isolate minute amounts of radium from tons of uranium ore [4]. This acknowledgment was not only a tribute to two professional chemists but also to other Polish Positivists among whom Marie Skłodowska-Curie grew up [5].

Years of formation

Marie Skłodowska-Curie was born in Warsaw. Her father, Władysław Skłodowski (1832–1902) taught mathematics and physics at high schools for boys, whereas her mother Bronisława neé Boguska (1837–1878) was headmistress of a reputable school for girls. It is worth remembering that they worked and raised their 5 children (of whom only four reached maturity) at the time when Warsaw, along with the whole North-Eastern territory of the former Polish Commonwealth, for more than 70 years had been subjugated to the Russian Empire [6]. Marie Skłodowska spent her childhood and youth under political coercion which had lasted since the ill-fated November Uprising (1831–1832) against Tsar [7], and escalated after the tragic January Uprising (1863–1864). At the same time Marie was a witness and a participant of the emerging intellectual and social movement known as Polish Positivism [8]. Marie's parents could serve as live examples of this movement.

In her autobiographical notes [9], Marie Skłodowska-Curie emphasises the influence of her wise and loving mother on the early formation of her character. After the premature death of his wife Władysław Skłodowski took over the whole responsibility for further development of his children. It was the father who showed the little Marie the beauty of sciences, fostered her deep patriotism and opened her mind to the whole European culture. This progressive man had no doubts that his talented daughters can and ought to be educated to the same extent as their equally gifted brother. The task was perfectly feasible up to the level of the high school. Further professional development of the young Skłodowski's ladies was hampered by the financial situation of the family and additionally by the fact that most European universities were not accessible for women yet. One of the scarce exceptions was the famous Sorbonne in Paris.

To raise funds for her studies abroad and to assist her elder sister in a similar objective, the 17-year-old Marie Skłodowska took her first job. She was working as a governess for the long six years, spending more than half of this time in the Szczuki estate, ca. 100 km to the North from Warsaw. During this whole period she strove for extending her knowledge: when she worked in Warsaw she adhered to the 'Floating University' – clandestine courses on natural and social sciences, organized by the Warsaw Positivists, and addressed especially to women. When she stayed in the countryside she had to learn on her own [10]. Thus, the 20-year-old Marie Skłodowska read treatises on sociology (in French [11] and biology (in Russian) [12], and studied the Text Book on Principles of Physics [13] by Alfred Daniell (1807–1897), freshly translated from English into Polish. All these books were brand new and very progressive, especially the last one. For instance, in the chapter on the constitution of matter, Daniell presented the John Dalton's (1766÷1844) atomic theory and commented on it in the following way: '*According to this view, matter consists of particles or atoms, each of which it is impossible with our present appliances to divide, and the division of which, if it were possible, would probably result in the subversion of our ides as to the apparently fundamental nature of some of the properties of matter*.' It is worth remembering that these words were written at the time when some chemists denied even the notion of the atom [14].

Having given up her fascination with social and natural sciences, Marie Skłodowska focused definitely on physics and mathematics. Due to self-instruction she had gained a decent theoretical background but desperately needed some opportunity to acquire experimental skills. Such opportunity came to her thanks to her maternal cousin Józef Jerzy Boguski (1853–1933) who in 1887 had organized the Physical Laboratory in the Museum of Industry and Agriculture in Warsaw [15]. When Marie came back to Warsaw, Boguski allowed her to use the lab's equipment and – what is interesting – he let her to perform experiments entirely on her own.

The Museum of Industry and Agriculture, established in 1875 by Warsaw Positivists, was a sophisticated form of national resistance. Its primary objective was education and promotion of new technologies amongst the rather poor and underdeveloped Polish society under Russian domination. Its more ambitious aim was to sustain the Polish scientific community, in opposition to the Imperial (thus, Russian) University in Warsaw, opened in 1870 [16].

The oldest division of the Museum was the Chemical Laboratory, created before 1875 by professor Napoleon Milicer (1842–1905) as a quality control laboratory for various customers [17]. Milicer was not only a top notch chemist but also a dedicated teacher. Assisted by Dr Ludwik Kossakowski [18] he was giving official courses on analytical chemistry and mineralogy, also for the Floating University students. Evidently, to such a course Madame Curie referred with gratitude many years later.

Scientists of the Middle, Eastern, and Western Europe

For the young compatriots of Marie Skłodowska-Curie the studies abroad were rather expensive but not so unusual. The mobility of Polish students rose after the defeat of the November Uprising in 1832

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when the Tsar Nicholas I (1796–1855) closed the Polish Universities: in Warsaw (established in 1816) and in Vilnius (established in 1579) [19]. Since then, smaller or bigger groups of Polish students could be met not only in Paris – the shelter of the Great Polish Emigration, but also in Zürich, Graz, Berlin, Riga, Tartu, Kiev, and in the capital of the Empire [20]. According to this trend, Władysław Skłodowski had gone to St Petersburg where he graduated from the Faculty of Natural Sciences. He was followed by Boguski, who later became an assistant of Dmitri Ivanovich Mendeleev (1834–1907). In turn, Milicer learned chemistry at the laboratory of Robert Wilhelm Bunsen (1811–1899) in Heidelberg [21]. By the way – a visiting scientist in the Bunsen's laboratory was once Mendeleev. Thus, through the upper middle class of her native Warsaw, the young Marie Skłodowska was exposed to the Mid-European (mainly German) scientific school characterized by methodical approach and comprehensive studies. This approach played a crucial role in her further research.

Another mainstay of the Polish intellectual life in the 19th century was the philosophy of the French Enlightenment. This fact was essential when Marie Skłodowska was making her final decision about going to Paris, the heart of French rationalism. She enrolled to the Sorbonne in the fall of 1891 and completed – *summa cum laude* – her studies in physics and mathematics in less than 3 years. Soon after, she met Pierre Curie (1859–1906) – an unassuming but already renowned professor of physics at the School of Industrial Physics and Chemistry (EPCI) in Paris – and married him in 1895. Thanks to the director of the EPCI, Paul Schützenberger (1829–1897) she received her first research grant [22] and some space in the lab. Since then she began to look for the subject of her doctoral research.

„The subject was entirely new …"

The subject emerged in 1896 in the nearby Museum of Natural History where Henri Becquerel (1852–1908) discovered penetrating 'uranium rays' which blackened photographic plates without previous exposure to light. After having described the basic properties of the newly discovered radiation [23, 24] Becquerel abandoned the theme and joined a rather large group of scientists who studied the X-rays discovered by Wilhelm Conrad Roentgen (1845–1923) in 1895.

Just contrary, Marie Skłodowska-Curie intuitively regarded the nature of uranium rays as a fundamental problem. She decided to study them by measuring their ionizing strength, which would be much more accurate than observation of photographic plates. And she was lucky: Pierre Curie had a quadrant electrometer with a piezoelectric balance, which could measure weak, less than pA, electric currents. Marie equipped this apparatus with a prototype ionisation chamber and began to measure the conductivity of the air around the samples, at fixed geometry.

Having methodically measured all available forms of the known elements she found that radioactivity is the atomic feature of uranium and thorium, independent from external factors [25]. Statistically significant discrepancies from the proportionality between uranium content and radiation strength made her suspecting the existence of another, more radioactive element. Basing on the accuracy of the available analytical methods, she estimated that its content in minerals must not exceed 1%. Nevertheless, she hoped to find it in uranium ores mined in Bohemia.

Uranium exploitation technology

Before the atomic era uranium was exploited mainly to produce staining additives to decorative glass or pigments for ceramics [26, 27].

Since the very beginning, industrial processing of uranium ores [28] has been based on alkaline and acid leaching of soluble UO_2^{2+} salts.

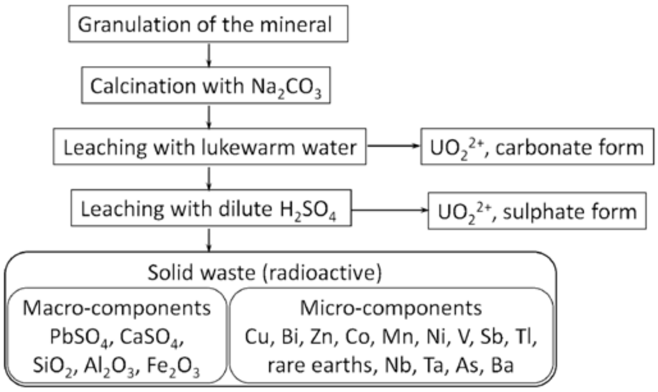

Fig. 1. Leaching of uranium ore [29]

In search for the hypothetical element in the unprocessed pitchblende, Marie Skłodowska-Curie performed the classical chemical analysis. She treated the ore with concentrated hydrochloric acid and then she precipitated insoluble sulphides, a part of which could be dissolved in ammoniac solutions. The final insoluble sulphide fraction contained bismuth and its highly radioactive analogue which Marie called Polonium. In the summer 1898, the Curies separated these sulphides by distillation [29].

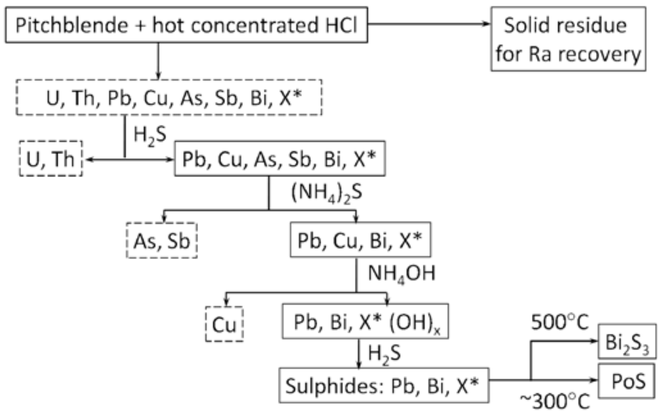

Fig. 2. Polonium separation scheme [29]

Industrial leaching of the pitchblende with sulphuric acid yields insoluble waste which is radioactive too. Working with it, Marie Skłodowska-Curie performed a titanic work of converting insoluble sulphates into soluble chlorides via carbonates. The industrial waste turned out to contain a radioactive analogue of barium. The Curies called it radium and announced its discovery in December 1898 [30]. Initially, radium and barium were separated by fractionated crystallization of their chlorides. When radium became very popular, Marie Skłodowska-Curie added extra purification steps into the original procedure and replaced chlorides by bromides in the final refinement.

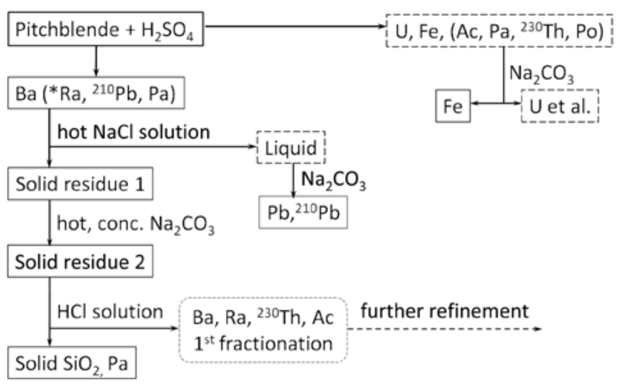

Fig. 3. Radium extraction from the pitchblende [32]

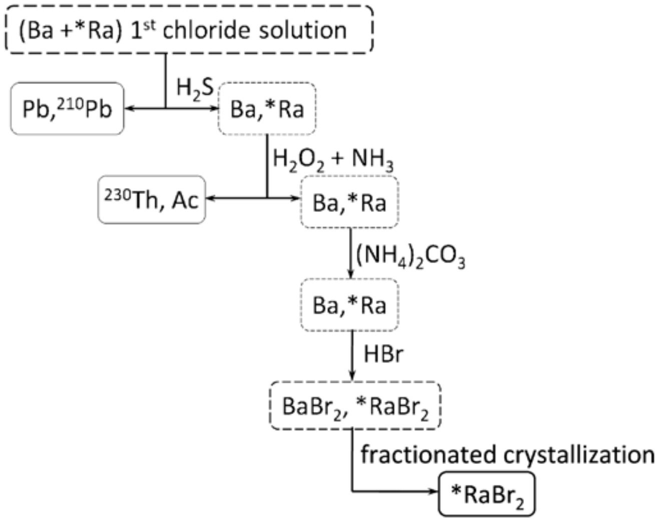

Fig. 4. Radium refinement scheme [32]

Within a few years, Marie Skłodowska-Curie fulfilled all chemical criteria to prove the discovery of radium: she assigned it to the proper group of the periodic table, determined its atomic weight (by means of argentometry) [31], produced samples large enough for atomic emission spectroscopy [32], and finally, she isolated metallic radium (electrochemically) [33].

Two Nobel Prizes and their meaning

One year after having isolated metallic radium Marie Skłodowska-Curie was awarded the 1911 Nobel Prize for Chemistry. The verdict of the Nobel Committee emphasized her achievements related to radium but said very little about polonium. Why? Because she could not prove the existence of polonium by means of classical methods. It was so because in secular equilibrium polonium concentration in uranium ores is only 74 ppb, compared to 340 ppm of radium [34]. Thus, the only proof for the existence of polonium was its radioactivity. But this way Madame Curie had given to chemistry and related sciences a powerful analytical tool: the method of radioactive tracers.

The 1911 Nobel Prize for Chemistry acknowledged Marie Skłodowska-Curie's discovery of the 'remarkable' radium which was not only radioactive but also beneficial to humanity. Eight years earlier, the 1903 Nobel Prize for Physics awarded to Becquerel and the Curies, acknowledged the 'subversion of views on fundamental properties of matter' anticipated once by Daniell. This subversion began with the Marie Skłodowska-Curie's doctoral thesis [35]. Since she had proven the existence of atoms which emit radiation and particles, the classical concept of elementary, everlasting, indivisible and invariable atoms was shaken. Later, the discovery of isotopes [36, 37] questioned the other assumptions of the classical atomic theory.

Pierre Curie was the first who recognized the importance of his wife's investigations and who joined her in her research. The Curies had noticed that radium salts glow, excite glass fluorescence and emit considerable amounts of heat [38]. This behaviour – apparently contradicting the energy conservation law – has been explained by the Curies in the most simple and logical way: radium atoms must have a great pool of internal energy. The value of this energy, estimated from the heating rate and the mean lifetime of radium atoms, turned out so huge that Pierre Curie warned in his Nobel Lecture about possible abuse of radium. Indeed: the typical combustion heat is about 4.1 eV per carbon atom, whereas the kinetic energy of radium alpha particles is 4.8 million eV per atom. Moreover, radium is a parent of 8 lighter nuclides (^{226}Ra 1600a, $\alpha \rightarrow {}^{222}$Rn 3.8d, $\alpha \rightarrow {}^{218}$Po 3m, $\alpha \rightarrow {}^{214}$Pb 27m, $\beta \rightarrow {}^{214}$Bi 19.8m, $\beta \rightarrow {}^{214}$Po 0.16ms, $\alpha \rightarrow {}^{210}$Pb 22.3a, $\beta \rightarrow {}^{210}$Bi 5.01d, $\beta \rightarrow {}^{210}$Po 138d, $\alpha \rightarrow {}^{206}$Pb), each of which releases a similar amount of energy. This impressing energy scale had not been extended until the discovery of the nuclear fission in 1938 [39].

Woman of genius

'Women of genius are rare' wrote the young Pierre Curie with a note of melancholy [40]. Unexpectedly, he met Marie Skłodowska. A key feature of Marie's genius was her ability to draw surprising but extremely logical and verifiable conclusions from the observable facts. For example:

In 1911, at the first Solvay Congress which was devoted to radiation phenomena and quantum theory [41], Marie Skłodowska-Curie formulated the opinion that radioactivity originates from a deeper, yet experimentally unavailable, part of the atom. In the same year Ernest Rutherford (1871–1937) discovered the atomic nucleus [42].

In 1913, at the second Solvay Congress [43], focusing on the Niels Bohr's (1885–1962) model of the atomic structure [44], Marie Skłodowska-Curie opposed the reversible ionization of atomic shells to the irreversible, destructive emission of beta electrons.

The third Solvay Congress, held in 1921, was devoted to atoms and electrons [45]. Then, Madame Curie postulated that: '*at short distances between the nucleus-forming particles some non-electromagnetic forces must be present* [46]. It was 11 years before the discovery of the neutron [47], and 14 years before the theory of nuclear forces [48].

Conclusion

Neither Marie Skłodowska-Curie, nor her husband expected that their analysis of the pitchblende would trigger a revolution in science. Marie simply wished to understand the nature of uranium rays. Pierre Curie – an outstanding experimentalist and a profound intellectual – did not hesitate to abandon his advanced research on magnetism for the pure love of further secrets of nature [49]. It seems that in science such attitude is the most rewarding.

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