W. J. KROLL: "A METALLURGIST OF THE UNUSUAL: THE AMPHIBIOUS AND RECALCITRANT LONE WOLF RESEARCHER"

John J. Moore

Head, Department of Metallurgical and Materials Engineering

Director, W. J. Kroll Institute for Extractive Metallurgy

Colorado School of Mines

Golden, Colorado 80401 USA

Introduction

William Justin Kroll was born in Esch/Alzette, Luxembourg in 1889. Although W. J. Kroll's name is most often connected with extractive metallurgy -- especially the production of ductile titanium and zirconium, his research interests and achievements span a wide area of process metallurgy, including age hardening alloys, improving the ductility and strength of both non-ferrous and ferrous alloys, grain refining, and purification of metals. Dr. Kroll's research achievements in the extraction of titanium and zirconium are well known. However, I would like to concentrate a little more in this presentation on demonstrating the other significant research achievements of Dr. Kroll -- achievements which indicate that he was indeed an extraordinary process metallurgist.

Professor F. D. Richardson of the Royal School of Mines, London, in his address in 1974, celebrating the centenary of the Colorado School of Mines and the dedication of the W. J. Kroll Institute for Extractive Metallurgy, stated that, "William Kroll's career is notable for the merit and originality of his work and for his great persistence". These three qualities best describe W. J. Kroll's approach to metallurgical research.

In his paper published in the Journal of the Franklin Institute in 1955, Dr. Kroll stated that, "in any invention of importance one is first to examine the educational background of the inventor and his mental preparation and development". William Kroll's educational background in metallurgy started as a small child. His father was a blast furnace manager and his grandfather an operator of an iron ore mine. He wrote of an early recollection: "a far-away picture still remains in my mind, when, as a child, in the darkness of a cold morning I was taken out of bed to light a new blast furnace with a bunch of cotton, impregnated with burning kerosene and fastened to the top of a long pole".

W. J. Kroll was a highly independent researcher who focused on industrial problems in a creative and innovative way. He was indeed a visionary in the process metallurgy field. He believed in the sound application of physical science principles and had a healthy regard for safety while conducting his experiments.

William J. Kroll was awarded the following honors for his outstanding work:

Student Medal - Technischen Hochschule

Perkin Medal - Society of Chemical Industry

Francis J. Clamer Medal - Franklin Institute

James Douglas Medal - American Institution of Mechanical Engineers

Heyn Medal - Deutsche Gesellschaft Fur Metallkunde

Albert J. Sauveur Award - American Society for Metals

Gold Medal - American Society for Metals

Castner Medal - Society of Chemical Industry (Great Britain)

Acheson Medal - American Electrochemical Society

Platinium Medal - Institute of Metals, London

Gold Medal - Institute of Mining and Metallurgy, London

Honorary Degrees from:

University of Brussels

University of Grenoble

Oregon State University

University of Missouri

Getting to Know Kroll Through His Quotations

In conducting the background research for this presentation, I feel the main resource from which I have become more acquainted with W. J. Kroll is from quotations that he has made in some of his early papers. One such quotation taken from his presentation on receiving the Perkin Medal Award in 1943 indicates how he felt about his profession. He writes, "it must have been quite difficult for the Perkin Medal Committee to define my true profession since metallurgists are of a complex nature and they might split, like some atoms, in various fission products. These splits may be physical, extractive, pyro, hydro, electro, thermodynamic, ferrous and non-ferrous, besides the many varieties of cross breeds with technologists. Having been wandering around in most of these groups, peeping in their melting pots, sometimes brazingly suggesting improvements in their methods while knowing very little about their art, I became in the course of the years somewhat amphibious and I am often perplexed when asked what my profession is. My answer may be, that I always use 'The metallurgist of the unusual'".

In reference to the above quotation, Kroll was mainly interested in the unusual or rarer metals. He goes on further to state that, "good metallurgists are not born. They are made with the ample money of the companies which hire them, and since they usually make their mistakes on a grand scale, they are the nightmares of business management".

A further quotation which indicates Dr. Kroll's approach to research and his belief in the independent researcher is also recorded here: "the fight of the individual with an independent mind against the collectivity in which he lives is as old as humanity, they will never cease to exist".

During the course of this presentation, I will use further quotations which indicate Kroll's humor and dedication to his work.

Kroll the Itinerant

Dr. W. J. Kroll was also somewhat of an itinerant in that he was born in Luxembourg in 1889, and studied at University at Charlottenburg in Germany from 1910 to 1917. He was employed by Metallgesellschaft in Frankfurt/Main from 1917 to 1919, moved to Vienna in 1919, and then Hungary between 1920 and 1921. He moved to Baden-Baden in 1922 and returned to Luxembourg in 1923. In 1940 he emmigrated to the U.S.A. to escape Hitler's invasion of Luxembourg. He remained in the U.S.A. until he retired to live near his brother in Brussels. Dr. W. J. Kroll died in 1973.

W. J. Kroll's Accomplishments

In order to appreciate the wide range of achievements of William Justin Kroll, it is interesting to chronologically list his investigations, developments, research findings and discoveries. Like all good researchers he used the knowledge gained through a previous investigation to implement and support the current and future research programs. This trend can be clearly seen in the following outline of Dr. Kroll's achievements.

The Early Years. From 1910 to 1917 Dr. Kroll studied at the Technischen Hochschule in Charlottenburg, Germany where he studied iron metallurgy and worked as an assistant to Professor W. Mathesius. He completed his doctoral thesis under the supervision of K. A. Hofman on the production of pure boron. He states that, "this influenced my future life deeply, for I never strayed far from the chosen field of preparative chemistry".

In 1917 he was employed by Metallgesellschaft in Frankfurt/Main and was sent to the lead refinery at Call/Eifel. There he developed a process for producing calcium-barium-lead bearing alloys by injecting sodium into a bath of lead containing barium and calcium chlorides. Figure 1 shows the schematic representation of his sodium injector from producing the calcium-lead alloy. He also worked on the development of a process to debismuthize lead and techniques to remove antimony and arsenic from tin alloys using aluminum.

Kroll's research work was not without certain disasters. One such incident was a huge fire initiated by the injection of sodium into the lead bath. He later commented that the skills which he developed from this incident would have fitted him well as a fire fighter in the London Blitz of the Second World War.

In 1919 he moved to Vienna to study a process from removing tin, silver, and gold from antimony-copper-tin residues produced from smelting church bells (a valuable materials resource in war time). Once he had developed the technology from this operation, he was recruited by the Hungarian government to build, with the help of personnel from the large Manfred Weiss, Csepel works, a plant from processing such church bell residues. The plant he constructed consisted of one shaft furnace, two converters, one reverberatory furnace, and an existing tin copper electrolysis plant.

Dr. Kroll recalls the first night of operation in which he was called out in the middle of the night on account of the bag house being destroyed by sulfuric acid present in the fumes. His response to this disaster indicates the man's ingenuity. With no immediate help available, he quickly solved the problem by sending someone to the local brewery to obtain cylinders of liquid ammonia to neutralize the bags by implementing a procedure of spraying the bags every few hours. Kroll's instructions to the bag house attendant was, "to apply to each chamber, after shutting it down and shaking the bags, enough ammonia until it started smelling".
The humor of W. J. Kroll is also noted in a quotation describing his observations of an important ceremony at the large Csepel works, he

states, "I had a great time at this plant, located on the island of Csepel on the Danube. This is because I had the opportunity of watching the work going on in this huge mill, which occupied at one time 20,000 workers. For instance, there was that job of casting new church bells for the next war. A German specialist was called upon and he started making molds and cores from manure, clay, and stale beer, a secret which had passed on from generation to generation in his family. These molds were then carefully dried after having been decorated with angels and pious inscriptions and works, exactly as described in 'Schillers Glocke'. My German had chosen a reverberatory furnace in which to melt these metals and to make his bronze, and he intended to cast a good dozen of bells while in operation. But he made his calculations without considering the oxidizing properties of his reverberatory furnace, which, as shown by the events, burned up the tin, forming a difficult fusible slag. The day of the great tapping all top figures of the city of Budapest had appeared, including the Admiral Horty and the Archbishop Prochaska. They were neatly dispersed around the furnace, in comfortable plush seats from which they could watch the pouring of the bells, which they had dedicated and which carried their name on a board wherever the molds laid buried on the ground. Meanwhile, my German was busy trying to get his metal out of the furnace, while one inspiring speech after the other was released until even the low quality spare ones were exhausted. Then came the moment when oxygen had to be put to work to save the situation to open the tap hole by chemistry. This operation was finally a success and the metal was gurgling happily out and filling the runners and molds, the latter, however, only partly, because too much metal had been burned up in the furnace. The faces of those, who had dedicated a bell and who had gotten only half of their deal, turned sour, and since nothing can be done with half a bell, they went home quite dissatisfied. But with much money spent in experiments, the company finally became experts in casting bells."

In 1922 Dr. Kroll left Hungary to set up a research laboratory in a small foundry in Baden-Baden. Here he developed a light weight, low expansion piston alloy which had good wear resistance and creep strength. This was a hypereutectic 23% silicon aluminum alloy with small additions of copper. He also developed a high creep strength magnesium alloy which contained mischmetall which was used in superchargers of aviation motors in World War II. This alloy was subsequently copied by U.S. metallurgists after examining planes that had been shot down.

<u>The Productive Years in Luxembourg.</u> In 1923 Kroll decided to return home to Luxembourg and to establish his own research laboratory in a large house (Figure 2) with one unskilled laborer, one mechanic, and one secretary who also performed some metallographic and spectrographic work. Of this venture, he is quoted as saying, "at that time such a project of a single man, working with his bare hands with only the wits of his mind had to be considered by a normal metallurgist as a kind of lunacy". However, this was a very productive period for Dr. Kroll. During this time he developed the process for debismuthizing of lead which was later commercialized by the American Smelting and Refining Company. He also developed a process for vacuum dezincing of lead produced from the Parkes

desilverization process. This process is outlined in Figures 3 and 4 and was later commercialized by W. T. Isbel of St. Joseph Lead Company.

Kroll also worked on age hardening of aluminum, in particular investigating substitutes from silicon, magnesium, and copper and developed a silver-aluminum alloy; a lithium-bearing aluminum-zinc alloy and magnesium-germanium-aluminum alloys. He also studied the germanium-aluminum phase diagram and the replacement of silicon with germanium crystals in radar detectors.

While working on fused salt electrolysis of beryllium, Dr. Kroll became beryllium poisoned in 1927 but stilI managed to develope the process for the reduction of anhydrous beryllium fluoride with magnesium.

It was at this time that Kroll became interested in the application of vacuum metallurgy in the extraction and purification of metals. Since he was not allowed into the local Heraeus plant he had to learn vacuum technology and methods by himself. He subsequently developed a process for the vacuum reduction of BaO with aluminum to produce barium metal, and the production of high quality calcium by vacuum sublimation of electrolytic grade calcium cast under an argon atmosphere. This period of work gave him the initial background for his subsequent development of titanium and zirconium extraction metallurgy.

The high purity calcium he produced in this period, he used as a reductant in a bomb reactor for the production of ductile chromium, vanadium, titanium, zirconium, uranium, and thallium. He also worked on the vacuum purification of silicon, copper, iron, chromium, beryllium, and alloys of copper, tin, and lead during this period.

In 1930 Dr. Kroll became interested in the reduction of titanium and initially investigated the reduction of $TiCl_4$ with sodium in a flash reaction process, but stated that this process would never become commercial on account of the high pressures created by such a reaction. He then looked at the reduction of $Ti0_2$ and ZrO_2 with pure calcium under an argon atmosphere in 1935.

In 1937 he started his first experiments on the pressureless reduction of $TiCl_4$ with calcium under an argon atmosphere and produced 250 grams (88% yield) of cold ductile titanium. On July 30, 1937 Dr. Kroll first experimented with the use of magnesium as a reductant for $TiCl_4$, eventually producing titanium of 180 Brinel hardness using a large stainless steel reactor. On July 13, 1938 he produced zirconium from a similar reaction involving zirconium chloride reduced with magnesium using the same equipment, and vacuum separation of the sponge zirconium from the surplus chloride.

In the Autumn of 1938 W. J. Kroll visited the U.S.A. in an effort to sell his titanium reduction process taking his titanium samples with him (Figure 5). Unfortunately, he found no interest and "left the United States in a sad state of mind, not having been able to interest anybody in my ideas".

While working on his main projects, Kroll was frequently interrupted to examine other process metallurgy areas. A sample of these include: iron-beryllium age hardening alloys; partial substitution of nickel for beryllium for providing increased hardness and grain refining; substitution of titanium or aluminum for beryllium in nickel-steels to produce age hardening; the use of chromium to provide hardenable stainless steels; and the precipitation hardening of Mg + C in nickel alloys, -- this was later taken up by the International Nickel Company in 1932.

Dr. Kroll also spent a large amount of his time investigating the purification of metals. In particular the vacuum distillation of chromium, manganese, beryllium, iron, tin, zinc, lead, and their alloys.

The USA Years. On February 10, 1940 William Justin Kroll emmigrated to the U.S. from Luxembourg, two months ahead of Hitler's invasion of his country. He stated, "I have abandoned all of my belongings, the whole equipment of my laboratory, and the big estate. Luck was with me since I got it back again in 1947, almost intact".

From 1940-1945 Dr. Kroll worked in the Union Carbide Research Laboratories at Niagara Falls as a consultant. In his own words, "this was a fertile time". He investigated diffusion electrolysis with soluble and insoluble anodes to produce iron, chromium, and magnesium powders; the production of anhydrous chlorides of magnesium and zirconium; the use of chlorides reacted with powdered solid alloys to extract unwanted constituents, such as copper from Monel metal and iron from iron-nickel; the separation of tantalum and niobium by hydrogen reduction of their oxides; the reduction of uranium oxide with calcium; the silicothermic reduction of magnesium; the production of electrolytic calcium; the production of sodium from NaCl using silicon and lime in vacuum.

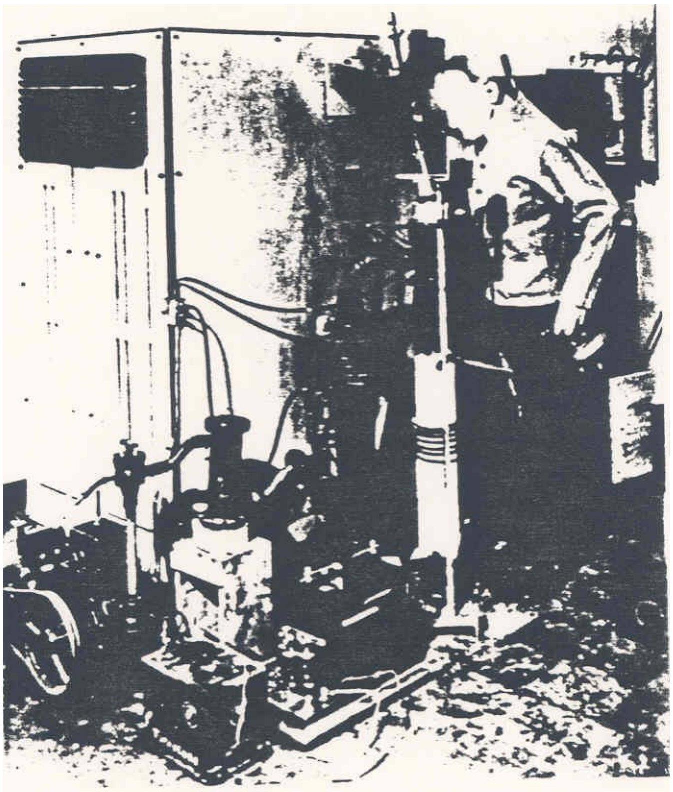
In December 1945 he joined the U.S. Bureau of Mines Albany Research Laboratory and took over the zirconium research program having spent the previous 18 months as a consultant on this project. In August 1946 he was able to roll the first strip of zirconium (Figure 6) ably assisted by Dr. A. W. Schlechten, who later became Head of the Department of Metallurgical and Materials Engineering, the Colorado School of Mines and the founding Director of the Kroll Institute of Extractive Metallurgy.

It was indeed fortunate that Dr. Kroll's ingenuity and research expertise in process metallurgy had been utilized in order to make zirconium available at the time when it was needed for the first atomic submarine reactor.

In 1950 Dr. Kroll resigned from the U.S. Bureau of Mines to work as a private consultant from his home in Corvallis, Oregon. During this period, Dr. Kroll's titanium patent was subjected to a long period of litigation before he was awarded all the royalties from titanium produced from his process. This legal process had a detrimental effect on Kroll's health. In 1965 he moved to a suburb of Brussels to be near his brother, Theodore, but continued his close association and friendship with Dr. A. W. Schlechten at the Colorado School of Mines.

A Final Comment

Dr. Kroll died in 1973. All through his professional lite he was insistent on the need for independent researchers to be allowed to conduct their research. In this respect he commented, "we have to offer the recalcitrant lone wolf researcher a kind of an asylum, since this useful species is lately menaced by extinction". It is, in fact, fortunate that this particular lone wolf researcher had the commitment to pursue his dreams and, in so doing, the world of metals and metals production is immensely the richer. Dr. Kroll's final sentence in his presentation on receiving the Perkin Medal from the Society of Chemical Industry in 1943 actually summarizes his great satisfaction in conducting research of the unusual, "I am happy that a gracious fate has allowed me to carry, for a while, the flag of rare metals research, around which many young men have now gathered to carry on, where I have left off".



Dr. W. J. Kroll working in his laboratory.

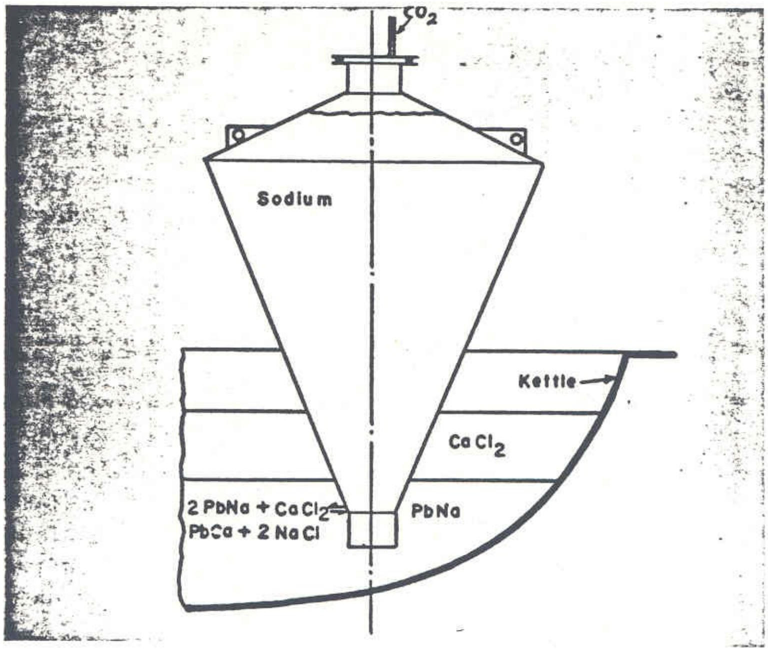


Figure 1 – Schematic representation of sodium injector for producing Ca-Pb.

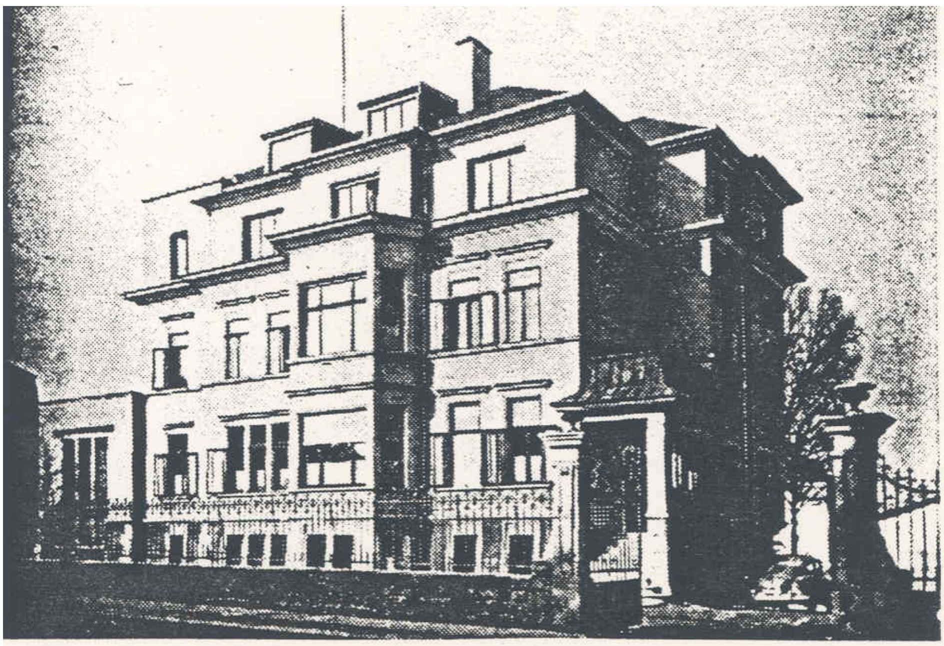


Figure 2 – Kroll's laboratory in Luxembourg.

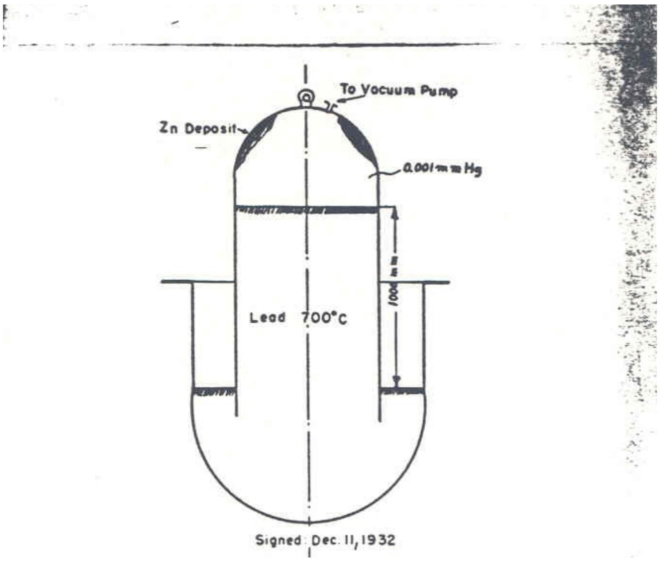


Figure 3 - Vacuum dezincing of Parkes lead (submerged bell jar).

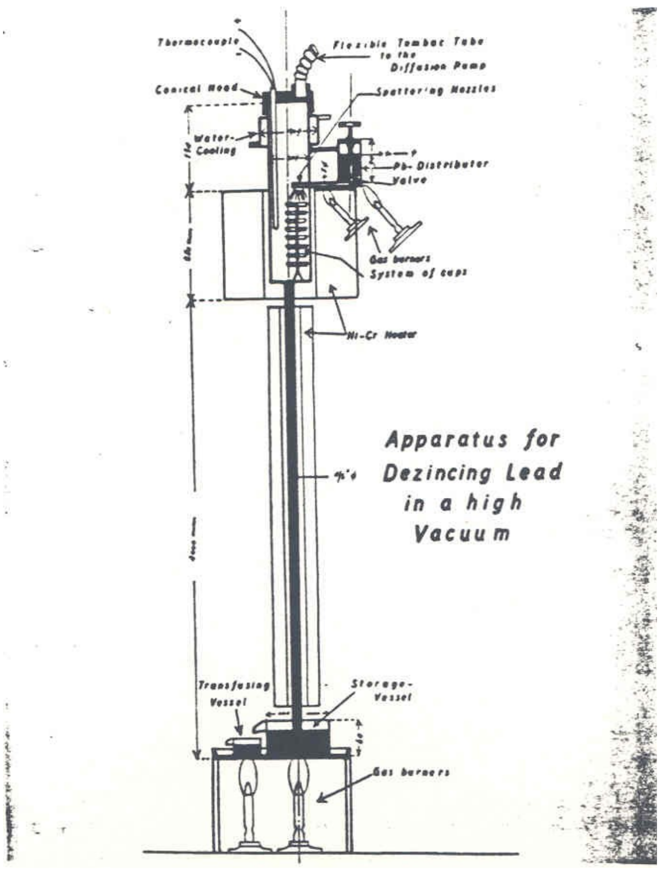


Figure 4 - Vacuum dezincing of Parkes lead (circulation and lead spray).

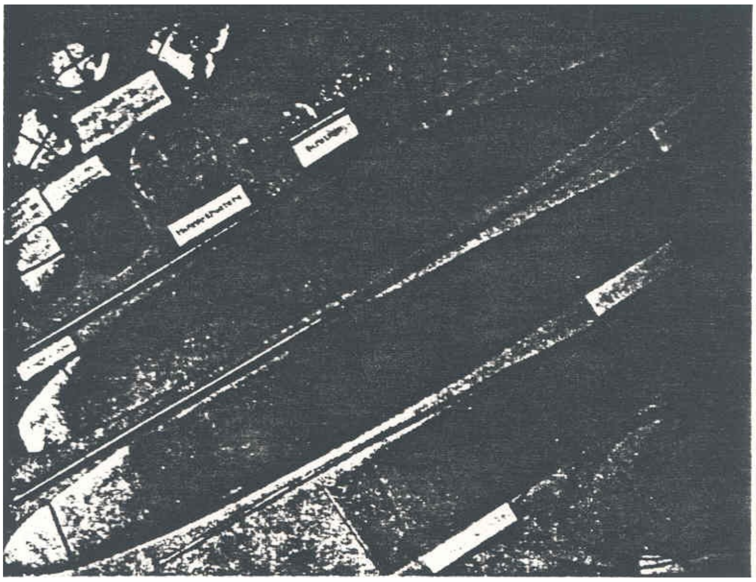


Figure 5 - Kroll's titanium samples produced in 1937.

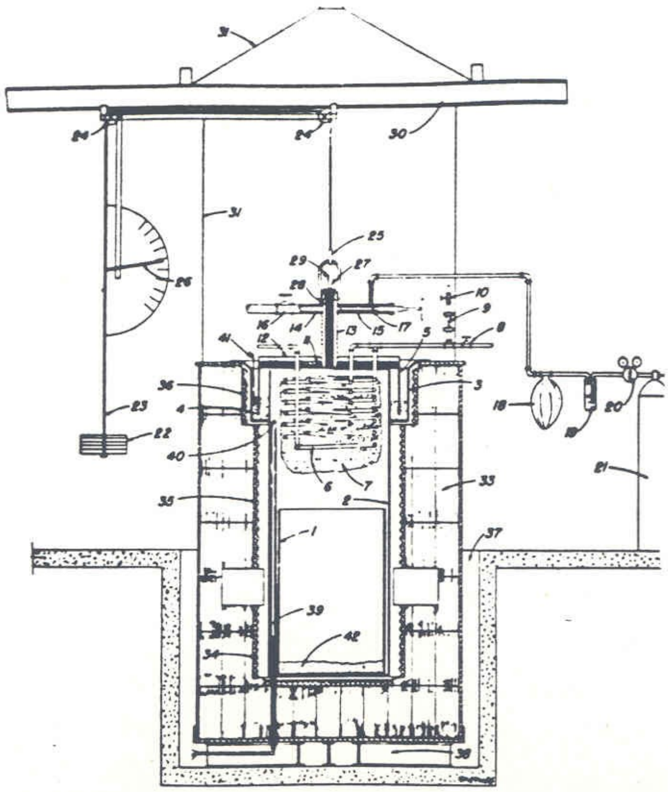


Figure 6 - Commercial equipment for zirconium extraction (USBM).