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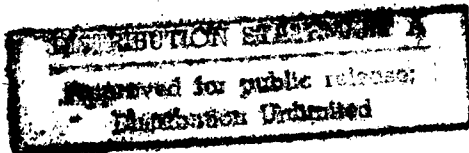
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PLUTONIUM PRODUCTION AT MARCOULE

- FRANCE -

by F. G.



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PLUTONIUM PRODUCTION AT MARCOULE

[This is a translation of an article written by F. G. in Industries Atomiques (Atomic Industries), Vol III, No 9/10, 1959, pages 99-102]

M. Pierre Couture, General Administrator of the CEA [Commissariat à l'énergie atomique; Atomic Energy Commission], during the Essen "Atom and Water" Exhibit, emphasized the importance of plutonium as a fuel in the [atomic] piles of the future. Hence it is particularly interesting to note that the CEA recently published details concerning the operation of the plutonium extraction plant M. Couture built at Marcoule.

M. de Rouville, Director of the Marcoule Center, in a recent issue of Bulletin d'informations scientifiques et techniques du CEA, remarked concerning plutonium [as follows]:

"Within a program limited in financial and industrial means and with less electric power made available by the facilities of this country than by those of large countries, the leading place at the start could only be given to this valuable product of uranium-238 nuclear transformation. On the credit side, plutonium has considerable theoretical advantages: its production is necessarily a part of the fission chain reaction development in natural uranium; it contains as much potential energy as uranium-235, so difficult to separate from its isotope 238; its use as a fuel ensures complete utilization of natural uranium without wasted energy; it is easy to separate it chemically from the other elements among which it takes form; producing it industrially calls for techniques similar to those required for its use as a fuel and, as a result, they can be used directly for fuel utilization. Selecting plutonium as the backbone of the first French five-year plan for the industrial chain based on the use of this fuel, beginning first with its production. For this purpose, half of the financial resources of the first five-year plan were devoted to the construction of the Marcoule Plutonium Production Center."

In the same issue, the Director of the Marcoule Center examines the reasons that the Marcoule reactors were built according to the known characteristics and their significance in the production of plutonium. He reminds us that "the principle used at Marcoule is based on the ability of an organic solvent to dissolve the products to be separated in very different proportions. The solvent used is tributylphosphate. The metallic mass is first entirely dissolved in concentrated and boiling nitric acid. All the elements go into the nitrate state. The nitric phase next makes contact with the solvent in a series of decanting mixers set up successively, the solvent phase circulating in opposite flow to that of the water phase in the oxidizing medium. The solvent first concentrates the uranium and the plutonium, leaving the fission products in the aqueous phase, making it possible to eliminate them. With them disappears the greater part of the beta and gamma activity, which call for the greatest protection against radiation. In the next battery, in the reducing medium, plutonium shifts from valence 4 to valence 3. In this form it is only slightly soluble in the solvent and goes back to the aqueous phase, through which it is separated from the uranium remaining in the solvent, together with the remainder of the fission products."

Such, in a few words, are the principles of operation of the plutonium plant. Subsidiary installations for the plutonium piles and for the plutonium separation chemical plant include a graphite-processing plant, installations for stripping irradiated fuel elements, and a station for treating liquid outflows. A total of 70 billion francs were spent in five years for the main and subsidiary installations of the plutonium production center. From 3,000 to 4,000 workers, technicians, and engineers worked on the location during these five years. The staff working the CEA plant increased from a few individuals in 1954 to 850 on 1 January 1958 and to 1,250 on 1 January 1959; it is expected to reach 1,700 by the end of the year.

M. de Rouville concludes his report as follows:

"The construction of the Marcoule plant is due to the cooperation of the Atomic Energy Commission, Electricité de France, and French industry as represented by hundreds of firms large and small working under the leadership of three main firms acting as general contractors: Société des Forges et Ateliers du Creusot, for G-1; the Compagnie de Saint-Gobain for the plutonium processing plant; the Société

Alsacienne de Constructions Mécaniques for G-2 and G-3. Marcoule has taught much to all those who, working with the same aim, planned and built the plant. To those who work there, each day brings a harvest of data of great value for later achievements. When fully developed, the plant will produce annually a quantity of plutonium with an energy value in fission terms of 2.5 billion kilowatt hours. Thus the Marcoule Center will have attained the objective assigned to it."

The technical details concerning the plutonium extraction plant were furnished by M. R. Galley, Plant Construction Chief.

Plans for the plutonium plant were begun in June 1954; they were essentially based on the results obtained at the Châtillon pilot plant and on laboratory research conducted under the direction of the chemical department. Work on the Marcoule location began one year later. The joint efforts of engineers, technicians, and workers made it possible to begin dry runs by the end of 1957 and to put in the first load of irradiated uranium on 6 July 1958. A number of provisions differ from those originally planned. The main purpose of M. Galley's report is "to describe the changes which, according to later studies in the laboratories and the outcome of tests, had to be made and to determine what has been achieved after ten months of operation."

1. Dissolving

Operations for dissolving the irradiated uranium load are conducted discontinuously in 11N nitric acid brought to the boiling point. High dissolving speeds of about 130 kilograms per hour were noted; accurate regulation of the quantity of oxygen made it possible to reduce the average loss of nitric acid to 3.5 percent. A great improvement on that score was obtained by bringing in a certain quantity of distilled water to the top of the recombination tower during the first minutes the uranium is being attacked. This begins when the temperature of the acid reaches 85 degrees centigrade and the small quantity of water that evaporated before the acid boiled has not made it possible for the nitric acid to recombine. Serious losses of nitrous vapors occurred at the start, losses which were reduced appreciably by the addition of water. The essential difference as compared with expectations lies in the almost complete suppression of chemical stripping operations for all baskets of uranium of normal composition. With-

out appreciable risk, it is possible to bring a load containing several hundred grams of magnesium scattered among the uranium bars directly into the concentrated nitric acid.

2. Extraction

Extracting is done in three stages. For the first two stages (extraction of the uranium and plutonium with solvents and re-extraction of the plutonium in the aqueous phase after the latter has shifted from valence 4 to valence 3 through the use of a reducing agent), the following operations were planned: first extraction--six extraction stages, one stage of dilution washing, two stages of nitric acid washing; second extraction--13 stages of re-extraction, two stages of tributylphosphate washing. The large number of stages in the second extraction was planned because of the difficulties in recovering plutonium at the Châtillon pilot plant. Hydrazine had first been selected as a reducing agent, but later ferric sulfamate seemed better adapted for re-extraction of solutions with greater concentrations of plutonium. But since ferrous ions had been a source of difficulties during the plutonium concentration stage that followed the use of a new reducing agent at the end of 1957, uranium sulfate was found to be as efficient as ferrous sulfamate and solved the problem of choosing a reducing agent. Since it introduced in the battery no new metallic ion, it solved at the same time the problem of precipitation and that of safety in recovering the plutonium.

Under these conditions, a new stage distribution between two extractions could be planned to increase the number of stages of the first extraction to the detriment of stages in the second extraction. By increasing the number of nitric washing stages in the first extraction from two to six, an appreciable increase in the decontamination factor through the improvement of nitric washing was obtained. The full factor of gamma decontamination established over a long period of operation ranges between 3×10^3 and 5×10^3 , or ten times the value that would have been obtained with two stages of washing. The new distribution is as follows: first extraction--seven stages of extraction, one stage of dilution washing, six stages of nitric washing; second extraction--eight stages of re-extraction, two stages of washing with tributylphosphate. The decision to bring about these changes was made in February 1958, at a time when the tests in the plant were already far advanced. The very complex modifications were made after six weeks of intensive day and night work.

3. Concentrating the Plutonium

Plutonium is concentrated in hanging decanters through precipitation with sodium carbonate and by dissolving the precipitate with nitric acid. This concentration is possibly only with a certain quantity of uranium acting as a precipitation primer. Following a few trial runs, the following processing method was adopted at Marcoule:

Sodium carbonate is first added in the decanter, followed by some 100 liters of diluted plutonium solution. During the homogenization phase, a determined quantity of uranium is introduced in uranyl nitrate form; next, by adding nitric acid, the pH value is adjusted from 12 to 10.8, which proved to be the optimum value to lessen losses in the mother liquor. Homogenization takes place in the revolving decanter; following decanting, the mother liquor is drawn and this operation is repeated six times before the whole of the precipitate is dissolved again through nitric acid. The concentration factor is around 60 and the solution containing from 5 to 10 grams of plutonium per liter and 70 to 80 grams of uranium per liter is stored in an "Eversafe" tank--that is, a tank in which the criticalness of the plutonium can never be reached--before purifying.

4. Solvent Decontamination

Owing to the low activity of the bars coming from Châtillon or from EL-2, this important side of the problem did not appear clearly during the years of research work carried on before the Marcoule Plant was built. It was not until the first measures were taken at the end of 1956 that it was apparent how acute it was. Besides washings with sodium carbonate, an installation comprising two leaded columns was set up: in the first, one washing and one decontamination of the solvent with a solution of sodium carbonate at 70 degrees centigrade is carried out; in the second this solvent is reacidified by washing with nitric acid 1N to bring it back to the required free acidity or 0.2N before it goes back into the cycle. After the first months of operation, it was found that, in spite of the decontamination, the quantity of beta and gamma-emitting particles associated with the remaining mono- and di-butylphosphoric acids was too great to make it possible to reach appreciable factors in the second uranium-decontamination cycle. Thus the two cycles had to be made separately and only the solvent coming from a third extraction could be decontaminated in this installation.

5. Plutonium Purification

To obtain absolutely pure and decontaminated plutonium oxalate from the concentrated plutonium nitrate containing uranium, corrosion products, and a still appreciable quantity of fission products, a process covering three essential phases is used: decontamination through extraction with solvent; purification on resins; precipitation of the plutonium oxalate. As far as the first phase is concerned, processing takes place in two successive batteries of decanting mixers. These small batteries have been planned to allow for much extra capacity and designed so that possible interaction between the quantities of plutonium present in the different stages cannot take place. In the first battery, the total quantity of plutonium is extracted, about 5 grams per liter, and 80 grams per liter of uranium, from the solution through a solvent including 20 percent by volume of tributylphosphate. Six stages of extraction and three stages of rewashing with a solution of nitric acid 1.5 N give a decontamination factor of about 250. In the second battery, the plutonium is re-extracted in six stages through a solution of ferrous sulfamate and is rewashed with solvent in two additional stages to reduce the uranium, the contamination of which is now only about 0.3 grams per liter. In this way a decontamination factor ranging between 400 and 500 is obtained for this phase as a whole.

Purification of plutonium on ion-exchanging resins has been the subject of long and painstaking study. Difficulties found in using hydrochloric acid resulted in directing efforts toward purifying on resins in a nitric medium; a very careful selection of the resins to be used and very strict laboratory processing methods made it possible to reduce the number of stages of this purification. At present, it is done as follows:

- The plutonium solution is oxidized through the use of 100 grams per liter of sodium nitrate and the pH value is adjusted to 7N through concentrated nitric acid;
- The Dowex anion resin is fixed on column 1 x 4.50, 100 mesh (a 7-liter column can easily fix from 200 to 300 grams of plutonium by operating from bottom to top);
- It is washed from bottom to top with 200 liters of 7N nitric acid solution;
- It is elutriated through a solution of 0.35 N nitric acid flowing from top to bottom.

Plutonium oxalate is precipitated by fractions of about 5 liters of plutonium solution so as to precipitate only 100 grams

of plutonium at one time. Oxalic acid is added so that the concentration of free oxalic acid in the floating part will be 0.01 N, the free nitric acid being about 0.8 N. Maturing time takes a few hours and the concentration of plutonium in the floating liquid drawn from the containers of the centrifuge is only 20 to 50 milligrams per liter.

6. Metallurgy of Plutonium

Processing is done in two successive stages: the centrifugation cups, each containing 100 grams of plutonium oxalate, are taken to the fluorination oven, where this oxalate is first calcined in the air at 150 degrees centigrade for one and one-half hours. This is followed by fluorination in PuF_4 at 520 degrees centigrade for three hours in a current of hydrofluoric acid and oxygen. The metallic plutonium is brought out later in a high-frequency furnace; the first processing of the mixture of PuF_4 and calcium (30 percent surplus) considerably increases the yield, which averages above 98 percent.

In concluding his report on operations at the Marcoule plutonium plant, M. Galley points out that "one of the fundamental conditions, which also applies to all the chemical plants of atomic energy industries, is that tests must absolutely be blank tests for metal equipment, to prevent danger of breakdown and to make sure of the resistance of the apparatus, but also to make the most complete dry runs possible of chemical operations in the various parts of the installation so as to have full mastery over all factors. Live runs must be undertaken only when all the weaknesses that can be found have been eliminated. Whatever the legitimate impatience of the personnel may be, it is wise to accept this necessity; it is the surest guarantee of good operation."

Another matter to which the author calls attention is the following:

"In pursuing the fundamental research carried on by the CEA or by the special laboratories of private industry, as well as those carried on by chemistry and engineering, the concepts must be big from the start because, with these new techniques, the learning and adapting time is always much longer than expected. On the other hand, the problem of the education in the field of radioactivity of hundreds of operators and workers from various trades and occupations, who,

during one year of dry and live runs, mixed with the specialized personnel of the CEA's scientific management or of the general contractor, has been one of our main tasks and concerns, because this familiarization with utterly new concepts had important psychological repercussions. It is not an exaggeration to say that only an operator or worker familiar with these questions of radioactivity can be used during a test period. This situation calls for special training and selection in order to create the proper climate."

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