Nuclear Archaeology for Gaseous Diffusion Enrichment Plants

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Abstract

The field of nuclear archaeology aims to develop the methods and tools to verify past production of fissile materials for military purposes, which may become necessary to support the verification of future arms control agreements that envision deeper cuts in the nuclear arsenals. Techniques have been successfully demonstrated for reconstructing historic plutonium production, especially in graphite-moderated reactors, but nuclear archaeology for uranium enrichment has proven much more challenging. Gaseous diffusion was historically the most widely used technology for military production of highly enriched uranium (HEU). With the termination of uranium enrichment operations in the Paducah plant at the end of May 2013, all gaseous diffusion enrichment plants worldwide will have been shutdown. The experience with decommissioning some of these plants in the United States, the United Kingdom, and France has shown that they contain large amounts of uranium particles deposited in the cascade equipment, especially in the diffusers of every stage. In this article, we evaluate the potential of using uranium particle deposition to understand and reconstruct gaseous diffusion enrichment plant operating history. First, we use a squared-off cascade enrichment model to estimate the enrichment capacity of a reference plant. Then, using a cross-flow filtration model, we consider the mass of solid uranium particles deposited over time in the tubular separation membranes of the stage diffusers. Finally, we assess possible nuclear forensics techniques that can characterize these uranium deposits, including age-dating analysis of statistically sampled particles, as a tool to reconstruct the operating history of the plant.

1. Introduction

Gaseous diffusion is an isotope separation method based on the molecular diffusion of a gaseous isotopic mixture through porous barriers (or membranes). In the case of uranium isotope separation, the processed gas is a mixture of U-238 and U-235 in uranium hexafluoride, UF_6. Gaseous diffusion was historically the most widely used uranium isotope separation method for the military production of Highly Enriched Uranium (HEU) in Nuclear Weapons States (NWS). In the framework of nuclear archaeology,[1] and the development of new tools to verify the past production of nuclear fissile materials for military purposes in NWS, this article presents a novel approach to reconstruct the operating history of Gaseous Diffusion enrichment Plants (GDPs).
As of June 2013, all GDPs worldwide have been shutdown.[2] In many cases, decommissioning and dismantlement of those facilities is already underway, making the development of verification methods a timely and urgent matter before important information is lost or voluntarily destroyed during the dismantlement activities.

During the early decommissioning stages in the United States, the United Kingdom, and France, it was found that the plants were contaminated by large amounts of uranium solid deposits in the cascade equipment. The mass of these deposits can represent several metric tons of uranium at

various enrichment levels held up in the components of the plant.[3] The analysis of this large contamination could represent a tremendous source of information on the operating histories of GDPs, and largely motivated the study presented in this paper.

Consequently we developed a two-steps approach to reconstruct the production histories of GDPs. First we propose to use a simple mathematical model of a GDP cascade using a set of basic process parameters to assess the HEU production rate of a particular plant. Then we suggest that the nuclear forensics analysis of the uranium deposits found on contaminated equipment could lead to the recovery of the history of the plant operation. Knowing the HEU production rate and operating periods could give an approximation of the total amount of HEU produced in a particular plant, which could eventually be compared with production records.

To illustrate the methods and results, the French gaseous diffusion plant in Pierrelatte is used as an example throughout the article.

2. Model of the Pierrelatte Gaseous Diffusion Plant Cascade

The Pierrelatte gaseous diffusion plant was designed to produce HEU for the French nuclear weapons and submarine reactors programs. The plant produced its first batch of HEU in April 1967 and was shut down nearly thirty years later on June 30, 1996.[4] The military requirements for Pierrelatte were to produce a minimum of 600–700 kg of weapon grade HEU per year.[5] The plant was composed of four main units called *usines ("plants")* with each unit representing one step of a squared-off enrichment cascade. The first design projects from 1958 referred to a total of 2,500 stages for the four units.[6] The low plant (*usine basse* or UB) was fed with natural uranium in the form, and enriched UF_6 up to 2% U-235, the middle plant (*usine moyenne* or UM) up to 7%, the high plant (*usine haute* or UH) up to 25% and the very-high plant (*usine très haute* or UTH*)* to 90% and higher.[7] The waste stream coming out of UB has been reported to have a tails assay of 0.35%,[8] though a higher tails assay of 0.5% U-235 has been reported for the early years of operation.[9] In 1982, UB and 75% of UM were shut down after the civilian Eurodif gaseous diffusion plant, *George Besse* (GB), reached its full industrial production capacity.[10] Afterwards low-enriched uranium produced in the GB plant would be delivered to the Pierrelatte plant for further enrichment. Starting in 1984, the 1,328 stages of the three remaining plants (25% of UM, UH, and UTH) were operated every year on a seasonal cycle from April to October until the Pierrelatte plant was completely shut down in 1996. [11]

Every single stage in the Pierrelatte plant was made of a compressor, a heat exchanger, and two diffusers.[12] Each diffuser is made of thousands of small porous tubes. The two diffusers are connected together as shown on Figure 1. This configuration, which is equivalent to a single stage with internal recirculation, can increase the stage separation factor by 37.5% and the separative power by 89%.[13] The average separation factor of a Pierrelatte plant diffuser was reported to be 1.0014.[14] With the two diffusers design, the average stage separation factor would have been increased from 1.0014 to 1.00193.

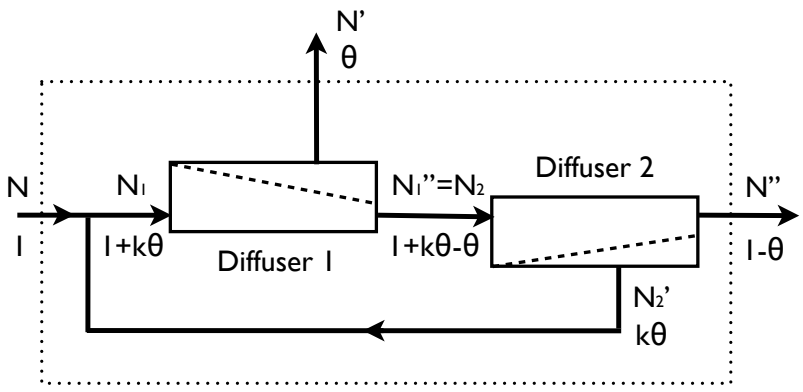

Figure 1: Stage with two diffusers. In this configuration, using k=1 and θ=0.5, the overall stage separation factor and the separative power are respectively increased by 37.5% and 89%.[15]

Each plant had its own type of diffusion barrier and stage compressor, all different from one another. All barriers in the plant were of the composite multilayer type: each tube was made of a thin porous layer which was deposited on top of a structural layer allowing the barrier to work in higher pressures.[16]

The following paragraphs focus on the low and the very-high plants as both are of particular interest in this analysis. UB gives information on the feed and the tail of the plant. The design of UTH is directly related to the weapon grade HEU product output of the plant.

The Low Plant (UB). The low plant started industrial production of LEU at a level of 2% in January 1965. The unit had a total of 480 stages in three 160-stages subcascades.[17] The material flow was equal in all stages until 1969 when the original square cascade profile of UB was gradually modified to better match the profile of an ideal cascade around the feed introduction stage (see Figure 2). [18]

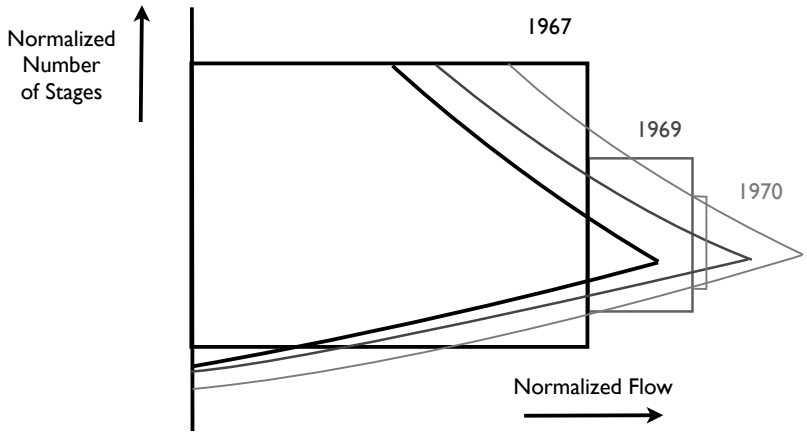

Figure 2: Historical squared-off and corresponding ideal cascade profiles of the low plant in the early years of the plant operation.

The UB compressor is reported to be a single stage 150-kW supersonic compressor with a mass flow rate of 5 kg of UF_6 per second[19] and a compression ratio of 8:1.[20] The equivalent uranium mass flow rate would be 1.07 x 10^8 kg of U per year.

The Very-High Plant (UTH). UTH was the final step in the enrichment process, thus its characteristics determine and constrain the product output of the plant. The material flow in UTH was reported to be 60 times less than in UB, which will give a flow of 1.78 x 10^6 Kg of U per year.[21] 1,150 compressors were used in UTH, one for each stage.[22] In June 1995, some of the first compressors installed in UTH started to run over 200,000 operating hours without failure.[23] Based on these values, the product rate of the plant can be estimated to about 580 kg of HEU per year. Assuming 200,000 hours of operation until June 1995, and adding 5,136 hours to account for further production until the Pierrelatte plant shut down in June 1996, a direct estimate of the total amount of weapon grade HEU produced at Pierrelatte would be 14 ± 2 tons of HEU. This amount is much lower than what was previously reported in the literature (i.e. 35 ± 5 tons of weapon-grade HEU).[24]

Results of the cascade model. The flow pattern in the Pierrelatte cascade is shown in Figure 3. The solid line represents the ideal cascade shape of the plant;[25] the dashed line, the equivalent squared-off cascade obtained with the parameters presented earlier.[26]

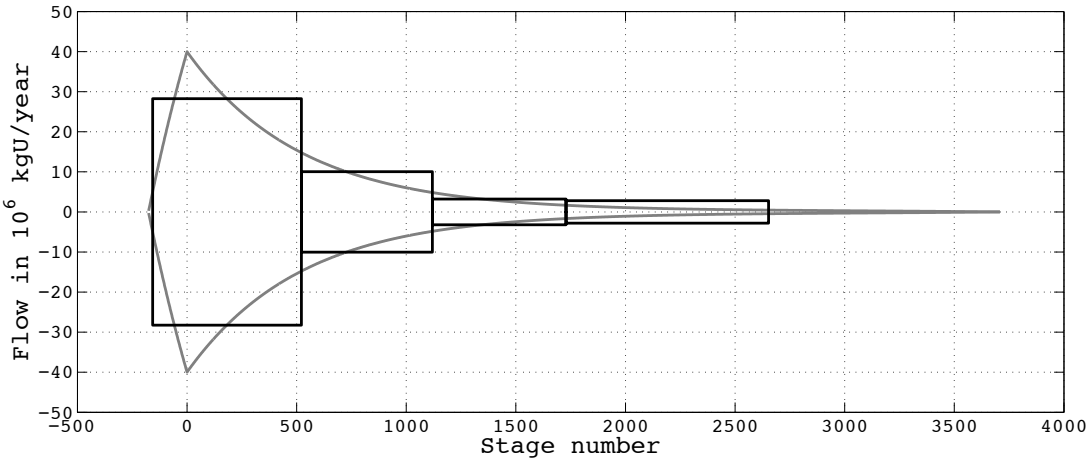

Figure 3: Pierrelatte ideal cascade and equivalent squared off cascade model.

Table 1 summarizes the results. This model represents only the production of HEU at 90% U-235 in Pierrelatte. It is important to note that the real capacity of the plant is likely to be higher, taking into account additional product streams at lower enrichment level. These product streams, used for example to produce LEU for naval reactor fuel, are omitted from the calculations due to the absence of information concerning them in the literature.

Table 1: Results of the squared-off cascade model for Pierrelatte in the early operational years. Product, feed and tail assays are respectively 90%, 0.7% and 0.5% U-235.

Plants	Number of stages	Material flow rate (10^6 kg of U per y.)	Separative power-SWU (10^3 kg per year)
Low	679	56.5	71.5
Middle	597	20.1	22.3
High	610	6.4	7.3
Very high	924	5.6	9.6
Total	2810	-	110.7

In what follows, we will study the origin of solid uranium contamination in GDP equipment, model the particle deposition mechanism in diffusers and assess the potential of using nuclear forensics techniques on deposited particle as a new tool to reconstruct the operating history of GDPs.

3. The Origins of Solid Uranium Contamination in GDP equipment

Uranium hexafluoride is a highly reactive molecule. Reduction of UF_6 during contact with exposed steel surfaces will produce various solid uranium compounds such as UF_4, UF_5 and $U2\ \ F_9$.[27] The hydrolysis of UF_6 by water is almost instantaneous and produces gaseous HF and solid particles of UO_2F_2. These reactions are not only a source of losses of UF_6, but are responsible for deposits and erosion in the plant equipment as well as the clogging of the separation barriers.[28] It is of the utmost importance for a viable plant design that the in-leakage of moisturized air or any type of lubricant oils in the process equipment is kept as low as possible, but contamination of the equipment is inevitable under realistic conditions and over longer periods of time. Among all the equipment, the diffusion barrier is the most sensitive to uranium deposition. Acting as a cross-flow filter, the porous membrane trapped most of the suspended uranium solid particles carried by the UF_6 flow (Figure 4).[29] In the Pierrelatte plant, 80% of the deposited uranium was located in the diffusers. After various chemical cleaning processes were used to remove most of the solid deposits, it was estimated that 3 metric tons of uranium at various enrichment level would not be recoverable and be disposed along with the associated process equipment in appropriate nuclear wastes storage facilities.[30]

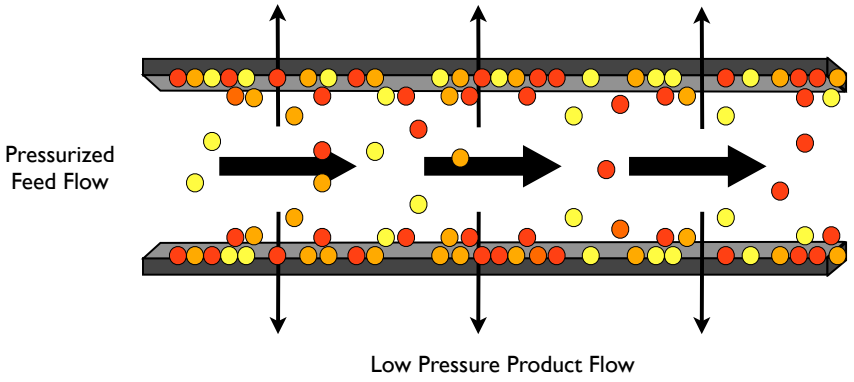

Figure 4: Suspension in cross flow: solid particles accumulation on the porous surface due to the influence of the large pressure gradient across the membrane.

4. Model of UO_2F_2 Deposition in Pierrelatte Diffusers

We are now interested in estimating the annual UO_2F_2 deposition rates in the stage diffusers of a gaseous diffusion enrichment plant in order to determine if methods of nuclear forensics can be used to reconstruct the plant throughput based on a particle deposition model and the data presented in the previous sections.

Model of UO_2F_2 deposition on a porous tubular membrane. The deposition mechanism of solid particles on the membrane is similar to the concept of cross-flow filtration. As UF_6 is processed in the diffuser, about half of the entering flow (corresponding to the stage cut) diffuses through the membranes. The pressure difference across the thickness of a porous tubular membrane induces a radial velocity that is responsible for the accumulation of solid particles in the boundary layer. Due to this phenomenon, micron-sized particles impact on the membrane and can remain trapped in the diffuser. Over time, an equilibrium thickness of the layer will be reached,[31] but away from this equilibrium, the rate at which the mass of deposited particles increases can be assumed to be linearly proportional to the particle concentration entering the diffuser,[32] the stage cut, and the volumetric flow rate of UF_6 in the tubular membrane. The particle deposition rate can be written as follows:

$$\dot{m}_{UO_2F_2} = \theta \cdot C \cdot Q_{UF_6} \tag{1}$$

with θ the "stage-cut", C the solid particles concentration and Q_{UF_6} the UF_6 volumetric flow rate.

UO_2F_2 particles concentration in the flow. The presence of UO_2F_2 is due to the hydrolysis of UF_6 by water when ambient moisturized air leaks into the process equipment. When HF obtained from this reaction comes into contact with oxides, it regenerates water leading to further decomposition of UF_6.[33] In the following, it is assumed that all water coming inside the process reacts with UF_6. In order to find the concentration of particles of UO_2F_2 in the UF_6 flow, several inputs are needed: the temperature, pressure and humidity of the air inside the process building as well as the in-leakage rate in the equipment.[34] For the Pierrelatte plant, two different values for the tolerated in-leakage allowed in the process (related to the flow of gas entering the equipment by porosity) were reported to be 2 x 10^{-2} and 10^{-4} liter-millitorr per second (lusec) and m^3 of volume occupied by UF_6.[35]

Actual deposition rate during the first two and a half years of operation. Between 1967 and 1968, about 2.5 years after LEU production started in Pierrelatte, all UB separation barriers were replaced. The official explanation was to improve the efficiency of the plant.[36] The 5.04 million disposed barriers tubes were buried in the ground on the plant site.[37] The barriers were contaminated by solid UF_5, UF_4 and UO_2F_2. The mass of deposited uranium per surface area was 10 to 20 g/m^2 with an enrichment level between 0.5% and 2% U-235. The mass was about equally distributed between the UF_5, UF_4 and UO_2F_2 when the barriers were buried.[38] Every barrier had a unit area of 235 cm² and a weight of 126 g.[39] Tube length is reported to be approximately 50 cm with 8 tubes giving the diffuser length.[40] Assuming 480 stages and two diffusers per stage, one diffuser would contain 5250 barrier tubes. The mass of deposited UO_2F_2

per single membrane tube can then be easily calculated and is found to be between 0.1 and 0.2 g;[41] giving a deposition rate of 40-80 mg of UO_2F_2 per year per tube of the Low Plant (UB).[42]

Expected UO_2F_2 deposition rate from the model. Using the tube geometry defined in the previous paragraph and a rate of air in-leakage in the process equipment equal to 2 x 10^{-2} lusec, we obtain a particle concentration of 3.6 x 10^{-12} kgm^{-3} of UO_2F_2 in the flow, which leads to a deposition rate of 0.13 mg of UO_2F_2 per year and per tube. This corresponds to the deposition of 5 x 10^7 one-micrometer diameter spherical particles of UO_2F_2 every year.[43]

5. Nuclear Forensics Analysis of the Deposited Particles

The previous results indicate that the large amount of UO_2F_2 particles trapped over time is sufficient to perform nuclear forensics analysis on barrier samples. If we assume that a certain number of porous tubes would be made available for analysis, we would expect to obtain relevant information even from a single tube, i.e., one out of several million tubes.

Bulk analysis of a selected tube would give information on enrichment levels, including U-235/U-238 and U-234/U-238 ratios, making it possible to locate quite accurately the position of the tube in the enrichment cascade. If several samples are available, they can be used to fit a squared off cascade model, allowing to obtain a good approximation of the cascade shape and normalized production rate. These results could be correlated for example with the mechanical analysis of a stage compressor to estimate the maximum production rate of the cascade.

The large available amount of uranium also allows performing the age-dating of the deposited particles using for example the Th-230/U-234 chronometer.[44] Figure 5 shows the predicted amount of U-234 atoms on a singular tubular membrane in UTH for three different scenarios. The first scenario represents the production scenario in Pierrelatte obtained from the literature (full production from 1967, then seasonal production from 1982 to 1996). The second scenario assumes full HEU production in Pierrelatte for the plant lifetime. The third one is a hypothetical scenario assuming constant production over lifetime and ending with the same U-234 inventory in 1996 as the second scenario. In the first case the Th-230/U-234 ratio is 4.09 x 10^{-5}, in the second 3.55 x 10^{-5} and in the third 4.09 x 10^{-5} as in the first scenario. A bulk analysis of the particles recovered from a single diffuser tube may therefore be sufficient to discriminate between different possible production histories and help confirm the correctness and completeness of a plant-specific fissile-material declaration.

Furthermore, if the forensic team has the ability to select individual particles or perform statistical sampling on a membrane, it would in principle be possible to reconstruct the complete production history of the stage and, by extension, the cascade. Each UO_2F_2 particle has a particular Th-230/U-234 ratio, indicating a particular time at which the cascade was operating. Therefore, the continuous contamination of the membrane during production will "store" the operating history in the deposited particle on the membrane surface. The time resolution needed to obtain a clear history would be of the order of 2–3 months, allowing the analysis to distinguish between production periods and longer-term shut-downs.

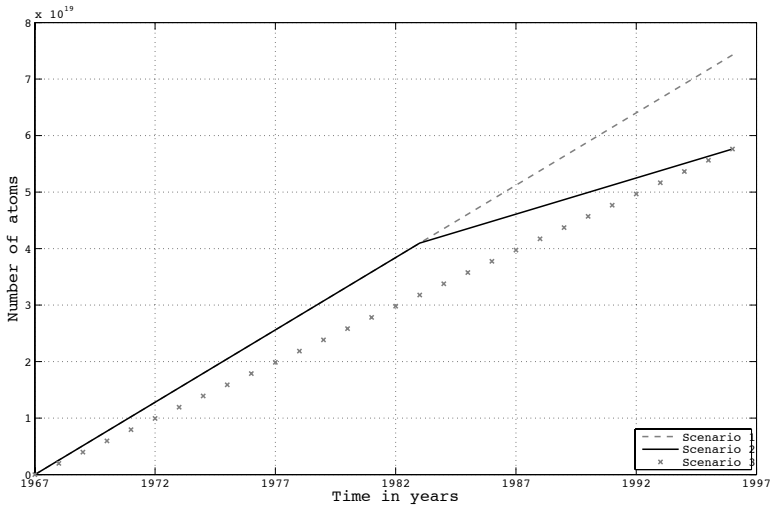

Figure 5: Quantity of U-234 on a single tubular membrane for three different scenarios. The solid line represents the declared production history in Pierrelatte. The dashed line represents the hypothetical full production for the plant lifetime. The crossed line represents constant production over lifetime ending with the same U-234 inventory as scenario 2.

6. Conclusion

This article proposes a new approach for the reconstruction of the operating histories of gaseous diffusion enrichment plants. Using a simple model for the reconstruction of a squared-off cascade and by evaluating the potential of a nuclear forensics analysis of the large amount of uranium deposited in the process equipment, especially in the diffusion barriers, it has been shown that it should be possible to make good estimates of a gaseous diffusion enrichment plant production capacity, including separative power and operating periods. These results can then be compared, for example, to material production records made available by nuclear weapon states as part of a transparency initiative or an arms-control verification regime. This would help build confidence on how much enriched uranium was produced in a particular plant.

During the dismantlement of a gaseous diffusion plant, the various types of cleaning processes, which are required to reduce environmental concerns, have a strong impact on the mass of recoverable deposits. Countries with dismantlement experience, could contribute to characterize this impact more precisely. The ability to access dismantled contaminated equipment is essential to perform any analysis. Traceability and transparency of the depository location where contaminated equipment are stored is therefore crucial. Since all gaseous diffusion plants are now shut down, it would be important for countries to keep some intact contaminated diffusion barriers for future analysis or to carefully characterize these barriers before disposition. Overall, the findings presented in this paper suggest that equipment from gaseous diffusion plants, especially the diffusion barriers, could be a unique source of information for future nuclear archaeology that would verify the completeness of fissile material production histories.

[1] Steve Fetter, "Nuclear Archaeology: Verifying Declarations of Fissile‐material Production," *Science & Global Security* 3, no. 3–4 (1993): 237–259.
[2] Operation of the George Besse I plant (Eurodif) ended in 2012, and the Paducah plants ceased uranium enrichment operation in May 2013.
[3] Pascal Bourrelier and Charles Kassel, "Le Démantellement des Usines Militaires de Pierrelatte," *Annales des Mines* (Juillet 1999): 37–43. (Reintroduce Reference)
[4] Bourrelier and Kassel, "Le Démantellement Des Usines Militaires de Pierrelatte."
[5] International Panel on Fissile Materials, *Balancing the Books: Production and Stocks*, Global Fissile Material Report, 2010, http://fissilematerials.org/library/gfmr10.pdf. Based on Daviet, *Eurodif*, p. 169.
[6] Jean-Pierre Daviet, *Eurodif : Histoire de l'enrichissement de l'uranium, 1973-1993* ([Anvers]: Fonds Mercator, 1993).
[7] International Panel on Fissile Materials, *Balancing the Books: Production and Stocks*.
[8] C. Frejacques et al., "Principal Results Obtained in France in Studies of the Separation of the Uranium Isotopes by Gaseous Diffusion," vol. 4 (presented at the The second United Nations international conference on the peaceful uses of atomic energy, Geneva, 1959), 418–421.
[9] KREBS, *Etablissement de Pierrelatte. Butte de Stockage: Reconnaissance et Etude d'Impact*, May 1998.
[10] Commissariat à l'Energie Atomique, *CEA Rapport Annuel*, 1962.
[11] Didier Chauvet, *Ordonnancement de la maintenance des usines de diffusion gazeuse et de la distribution électrique* (Etablissement de Pierrelatte: Cogema, April 19, 1990).
[12] Bourrelier and Kassel, "Le Démantellement Des Usines Militaires de Pierrelatte."
[13] Massignon, "Gaseous Diffusion."
[14] Bourrelier and Kassel, "Le Démantellement Des Usines Militaires de Pierrelatte."
[15] Massignon, "Gaseous Diffusion."
[16] Daviet, *Eurodif*.
[17] Ibid.
[18] C. Leduc et al., "Acquis Français en Matière de Séparation Isotopique," vol. 9 (presented at the fourth United Nations international conference on the peaceful uses of atomic energy, New York: UN, 1972), 15–29.
[19] Daviet, *Eurodif*.
[20] Frejacques et al., "Principal Results Obtained in France in Studies of the Separation of the Uranium Isotopes by Gaseous Diffusion."
[21] Daviet, *Eurodif*.
[22] "Cogéma: Le secret dévoilé," *La Tribune*, November 2, 1995.
[23] Ibid.
[24] International Panel on Fissile Materials, *Balancing the Books: Production and Stocks*.
[25]For the equations used to calculate the ideal cascade see Stelio Villani, *Uranium Enrichment*, vol. 35, Topics in Applied Physics (Berlin ; New York: Springer-Verlag, 1979).
[26] Equations used to produce the squared-off cascade are derived from the theory presented in K. Cohen, *The Theory of Isotope Separation as Applied to the Large-Scale Production of U-235* (New York: McGraw-Hill, 1951) and B. Brigoli, "Cascade Theory," in *Uranium Enrichment*, ed. Stelio Villani, vol. 35 (Berlin, Heidelberg: Springer Berlin Heidelberg, 1979), 13–54. In this

model, the criterion used to optimize the cascade shape consists to minimize the total flow rate of every step per mole of product.

[27] R.D. Scheele and al., "Development of NF3 Deposit Removal Technology for the Porthsmouth Gaseous Diffusion Plant," in *WMS Papers* (presented at the Waste Management Symposia, Tucson, AZ, 2006), www.wmsym.org/archives/2006/pdfs/6297.pdf.

[28] D. Massignon, "Gaseous Diffusion," in *Uranium Enrichment*, ed. Stelio Villani, vol. 35 (Berlin, Heidelberg: Springer Berlin Heidelberg, 1979), 55–182, http://www.springerlink.com/content/77l7l0224017k680/.

[29] G. Menard et al., CSL_CITATIOTangentielle des Gaz: É z: de la Formation du Dde l,de*Powder Technology* 71, no. 3 (September 1992): 263{"cit

[30] Bourrelier and Kassel, "Le Démantellement Des Usines Militaires de Pierrelatte."

[31] At that point, particles re-entrainment due to an increasing shear velocity at the gas/deposit interface balances the amount of newly trapped particles stopping further growth of the deposit layer.

[32] G. Menard et al., "Filtration Tangentielle des Gaz: Etude de la Formation du Dépôt," *Powder Technology* 71, no. 3 (September 1992): 263–272, doi:10.1016/0032-5910(92)88032-D.

[33] The impact of the water-regeneration cycle on the particle concentration is difficult to assess and remains unknown to the authors.

[34] The air temperature and pressure inside the process building are assumed to be 55°C and 1 atmosphere. No data on the air relative humidity was found. A value of 15% will be taken for the calculations assuming a relatively dry and monitored atmosphere in the process building.

[35] Frejacques et al., "Principal Results Obtained in France in Studies of the Separation of the Uranium Isotopes by Gaseous Diffusion"; Massignon, "Gaseous Diffusion."

[36] Commissariat à l'Energie Atomique, *CEA Rapport Annuel*, 1967.

[37] KREBS, *Etablissement de Pierrelatte. Butte de Stockage: Reconnaissance et Etude d'Impact*.

[38] Ibid.

[39] Ibid.

[40] Daviet, *Eurodif*.

[41] KREBS, *Etablissement de Pierrelatte. Butte de Stockage: Reconnaissance et Etude d'Impact*.

[42] This amount would be equivalent to 1.6×10^{10} one-micrometer diameter spherical particles trapped per year in every tubular membrane.

[43] This rate is about three hundred times smaller than the rate calculated from the buried first generation barriers. This indicates clearly that the process in the Pierrelatte plant was not working as designed or specified during the first years of operation. This eventually led to the replacement of all the tubular membranes (over 5 millions) in UB only 2.5 years after the production had started.

[44] A. Glaser and S. Bürger, "Verification of a Fissile Material Cutoff Treaty: The Case of Enrichment Facilities and the Role of Ultra-trace Level Isotope Ratio Analysis," *Journal of Radioanalytical and Nuclear Chemistry* 280, no. 1 (April 1, 2009): 85–90.