THE FRENCH APPROACH FOR MANAGEMENT OF DEPLETED URANIUM A CONSTANTLY IMPROVED TECHNOLOGY

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INTRODUCTION

The uranium enrichment industry generates large amounts of depleted uranium hexafluoride (DUF_6), as a by-product, whether using gaseous diffusion or centrifuge technology. About 1.2 million tons of U has already accumulated throughout the world since the beginning by the uranium enrichment industry. Future annual production rates are estimated between forty-five and sixty thousand tons of depleted uranium, depending upon the operational tails assay of the enrichment plants and the effective use of MOX fuel and down-blended HEU.

Depleted UF_6 is mostly stored as a solid in metal cylinders. But storage of depleted UF_6 may pose environmental risks: contact with moisture (in case of cylinder integrity defect) can lead to chemical reactions producing hydrofluoric acid (HF), a hazardous material. For long-term storage, the ideal solution is therefore to convert the depleted UF_6 into a stable, non-corrosive and easily re-usable form such as uranium oxide, and to sell it as much as possible to the commercial sector.

However, only a few hundred tons per year of depleted uranium are currently re-used, mostly included in MOX fuel for light water reactors. This application might be potentially extended in the future if the option of fast breeder or high temperature reactors is eventually developed for power production, when the earth ore and gas resources become scarce. Therefore, at least for the several decades to come, depleted uranium must be preserved as a potential energetic resource either because of its high fertile content (~ 99.7% U-238) or its remaining fissile content (~ 0.3% U-235). The challenge for the nuclear community is to secure a safe and reversible storage of depleted uranium during this period of time.

COGEMA provides uranium enrichment services to the nuclear industry worldwide. To meet general French safety requirements related to environmental protection issues, COGEMA has developed, as an extension of the enrichment operation, a facility to convert DUF_6 into a stable, fluorine-free compound.

After 5 years demonstration of the process on a pilot plant, COGEMA placed a facility in industrial operation in 1984 to convert DUF_6 into stable oxide U_3O_8 ; a second facility was commissioned in 1993, doubling the capacity.

Each year, the COGEMA plant allows to convert ("defluorinate") about 21,000 tons of DUF_6 into uranium sesquioxide (U_3O_8) and high purity aqueous hydrofluoric acid (70% HF). Up to date, about 220,000 tons of depleted UF_6 have been defluorinated. The U_3O_8 form allows safe interim storage of depleted uranium, as evidenced by about 20 years of COGEMA storage experience. The high purity aqueous 70% HF is sold in the European commercial sector under rigorous safety conditions.

Since the beginning of its industrial defluorination operations, COGEMA has ever been concerned to make its technology as reliable and as cost effective as possible. Accordingly, an improvement work has been constantly under way which already benefited to the construction of the second facility, completed in 1993. This paper will give an overview of the improvement work performed over the years, relating not only to the technology (optimizing the defluorination output, reducing the corrosion inside the kilns, improving the uranium oxide powder compaction factor...), but also to the process itself (hydrodynamic modeling of the process reactions inside the kiln) and maintenance issues (systematic monitoring of filters plugging, recycling of cartridge filters...).

COGEMA'S DEFLUORINATION PROCESS

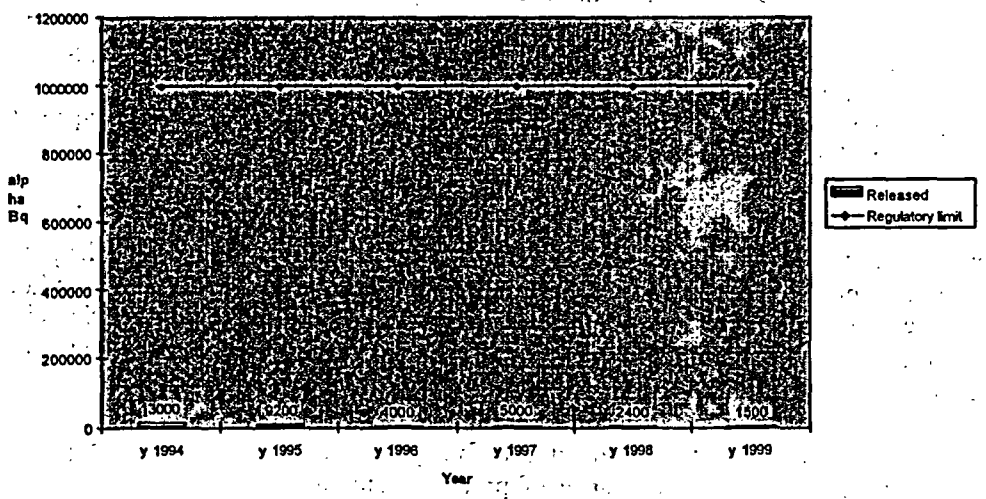
The basics of the process was already presented by COGEMA at several other U.S. conferences. The process will then be only summarized here in order to better emphasize on the technical improvements already undertaken.

Cylinders of depleted UF_6 are transferred from the enrichment facility and inserted into airtight autoclaves where UF_6 is turned to vapor using wet steam and is directed to the defluorination kiln. In the first part of the kiln, gaseous UF_6 reacts with overheated steam. The hydrolysis exothermic reaction generates intermediate solid uranyl fluoride, UO_2F_2 and gaseous HF. The solid UO_2F_2 falls into the second part of the kiln through a screw conveyor and reacts at a higher temperature with hydrogen and overheated steam. The conditions of this endothermic pyrohydrolysis reaction are optimized to produce a U_3O_8 oxide with a low residual fluoride content and a valuable co-product, hydrofluoric acid, which contains the excess water from the reaction.

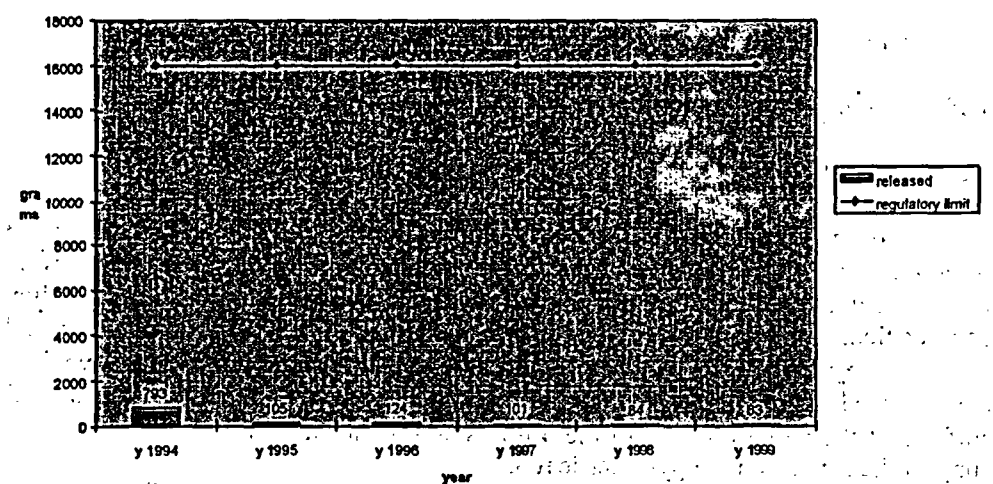
The mixture of hydrogen fluoride and steam leaves the kiln through a filtration chamber, which removes uranium oxide from the gas. This gas is then condensed and scrubbed in such a way that a 70 % HF is obtained. After monitoring, the HF is pumped to a dedicated storage area consisting of 20 m^3 tanks. The product is then transferred to road or rail tanks for final shipment to customers.

The CEA-COGEMA process is a dry process, which does not generate any liquid process effluent. Twenty years of operation have shown that its impact on the environment is very limited. COGEMA has patented an efficient filtration device at the exit of the defluorination kiln. As a result, gaseous releases are negligible and well under the regulatory limits for uranium and fluorine contents. And the chemical hazards associated with long-term storage of depleted uranium are reduced to a minimum by COGEMA's choice of the stable U_3O_8 form and the use of specially designed storage 10m^3 containers called DV70.

Gaseous Release from the COGEMA DUF6 defluorination facility - Uranium Content



Gaseous Release from the COGEMA DUF6 defluorination facility - Fluorine Content



THE FRENCH MANAGEMENT OF DEPLETED URANIUM: A CAREFULLY-PREPARED INDUSTRIALIZATION

Studies to convert DUF_6 into a stable, fluorine-free compound were started by the French Atomic Energy Commission (CEA) in the 1970s. Research focused on a dry process, to avoid the generation of undesirable liquid effluent, and on the production of uranium oxide with recovering of the fluorine component in a re-usable form. Various alternatives of the dry process were investigated. One process that received special attention was to distill the aqueous HF to obtain anhydrous acid and to recycle the remaining azeotrope by direct re-injection in the defluorination kiln. This alternative was eventually discarded since it required more sensitive kiln technology and was more corrosive.

The CEA registered a patent on its dry process. CEA's oxide product, preferred for its stability, low solubility in water and low corrosiveness, is sesquioxide U_3O_8, close to the pure chemical form of uraninite or pitchblende, the prevailing natural form of the uranium found in ore. The fluorine content is recovered in the form of marketable aqueous hydrofluoric acid (with a 70% HF content). The decision to industrialize the CEA process was concomitant with the beginning of construction of the EURODIF enrichment facility.

First, industrial feasibility was demonstrated for five years on a full-scale pilot plant. Important parameters, such as the resistance of process materials to UF_6 corrosion, were tested and optimized. In 1984, just two years after full commissioning of the EURODIF facility, the first COGEMA industrial defluorination unit started its operations in Pierrelatte (South of France). A second unit, benefiting of improvements from the operation experience of the first facility, was commissioned a few years later, in 1993. The full COGEMA plant today allows to process 21,000 metric tons of DUF_6 per year (14,000 MT uranium), yielding roughly 17,000 Mt of U_3O_8 and 10,000Mt of 70% hydrofluoric acid per year.

IMPROVEMENTS OF THE PROCESS TECHNOLOGY OVER THE YEARS

Examples of technological improvements

On the defluorination kiln :

- The corrosion of the kiln shell, due to high temperatures in the central section (~ 900°C) and very aggressive atmosphere (gaseous HF), has been extensively investigated. An optimization of basic parameters such as shell thickness, shell alloy composition, ... has allowed to reach a satisfactory technical and economical compromise with regard to the shell lifetime. Maintenance procedures have also been defined to reduce the corrosion of the kiln equipment: for instance, the annual shifting of the radial position of the 6 lifters and the axial position of the rings that support the lifters and the pyrometric rod.
- The geometry of the injection nozzle (for the UF_6, vapor and intermediate nitrogen flow rates) has been adjusted to prevent clogging at the end of the nozzle and to ensure an instantaneous UF_6 hydrolysis reaction inside the reaction chamber.
- In the second defluorination facility completed in 1993, the filtration unit located at the top of the hydrolysis chamber was re-designed to allow the integration of a systematic monitoring of filters plugging. Since then, studies have been performed for optimizing the counter-current unplugging cycle, in order to increase the lifetime of the filters.

- The air-tightness at the kiln ends has been increased, thanks to the use of especially designed materials and a torque wrench.
- The stroke frequency of the hammer placed at the exit end of the rotary kiln has been adjusted to prevent the very cohesive UO_2F_2 powder to stick on the walls of the kiln. Soon, additional vibrating devices will be set up on the external surface of the kiln to even more limit this sticking phenomenon. The positions of these future vibrating devices on the kiln surface will be determined by numeric simulation.
- Recently, a hydrodynamic study has started to characterize the flow pattern inside the hydrolysis chamber using Computational Fluid Dynamics. The aims are to optimize the working conditions in order to reduce plugging occurrences through a scientifically justified position of sensors (thermocouples, vibrating devices) and to tentatively control the size distribution and quality of UO_2F_2 aggregates.

Gas process :

- The condensers are designed to cool down the gaseous HF + H_2O + N_2 stream exiting the defluorination kiln through the filtration chamber. A close collaboration between COGEMA and the manufacturer of this equipment has allowed to design condensers with a geometry and a material structure specifically adapted to our technology requirements.

U_3O_8 collection :

- The performance of the U_3O_8 powder compaction unit has been increased by a factor of 40% over the years (up to a current average content of 10.5 Mt U_3O_8 per storage DV70 container). Improvements have included: adjustment of the scrappers conveying the powder to the rollers, monitoring of the input by adjusting the speed of the feeding screw, modification of the vibration table to increase the powder density inside the DV70 containers up to a value over 3.

HF processing and management :

- The 70% HF produced by the COGEMA defluorination plant is very pure thanks to an efficient patented filtration device at the exit of the defluorination kiln. Studies have been carried out to convert this 70% HF to anhydrous HF, which can be sold on the European market at a much higher price. Five different processes have been technically compared. Direct distillation has been discarded because of the lack of commercial market for the 38% azeotrope by-product and the problems associated with its direct re-injection inside the defluorination kiln (such as the design of a special super-heating system). The currently preferred process consists in liquid-liquid extraction but no investment decision has been taken yet due to the present very high demand on the European market for the high purity-grade 70% HF produced by the COGEMA defluorination plant.

Process modeling

Several PhD studies have been conducted for a better understanding of the phenomena occurring in the rotary kiln during the conversion of UO_2F_2 to an oxide. Most of this modeling research work is described in master's theses:

- The kinetics of the pyrohydrolysis reaction[1]
- The establishment of a model to describe the operation of the first CEA defluorination rotary kiln[2]
- The establishment of a numerical code describing the flow pattern inside the CEA kiln as well as the temperature and the composition of solids and gases at different axial positions[3]
- The establishment of a numerical model for the COGEMA defluorination kiln with the goal to describe as accurately as possible the various phenomena inside this kiln and to propose optimizing ways for working conditions and design of new kilns. The movements of solids in rotary kilns equipped with lifters was studied thoroughly; a method, based upon geometrical considerations, and on experiments, was developed to calculate the average distribution of powder in transverse sections of the kiln and the bed depth profile. A kinetic model was set up to calculate the conversion of solid at each axial position. The thermal conductivities of powder beds, the emissivity of walls and powders and some heat transfer coefficients were experimentally measured[4].

R&D on other "defluorination" processes

- Several reactions allowing to convert UF6 into U3O8 with a concomitant production of valuable fluorine products have been studied and tested at a laboratory scale. Interesting results were obtained for the reaction $UF_6 \rightarrow SiF_4$, but none has been implemented due to a large number of secondary problems.

CONCLUSION

Owners of depleted uranium have the responsibility to store it safely and minimize the risk of chemical hazards. COGEMA safely removes the fluorine component from DUF_6, recovering fluorine in the form of an easily marketable product and rendering the uranium into a stable oxide appropriate for safe storage and easy re-use in the nuclear fuel cycle or any other potential application. In more than 16 years of industrial experience, COGEMA has optimized the operational parameters and the preventive maintenance program of the defluorination facility, making this operation not only safe, but also cost-effective by increasing the service life of many process equipment. As exemplified by this paper, a pro-active R&D approach has been followed by COGEMA over the years in a constant concern to better manage the technical issues associated with the implementation of a simply-written process in aggressive reaction conditions. Even now, new R&D programs are under way or in project.

[1] P. FAVRE PhD Thesis, Claude Bernard University, Lyon (France), June 1977
[2] P. MUREAU PhD Thesis, Institut National Polytechnique de Toulouse, July 1992
[3] S. BOUTIN-LA COMBE, PhD thesis, Rouen University (France), March 1995
[4] M. DEBACQ, PhD thesis, Institut National Polytechnique de Nancy (France), January 2001