

**AREVA/COGEMA MANAGEMENT OF DEPLETED UF₆
300 000 t dUF₆ DEFLUORINATED
LESSON LEARNED**

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ABSTRACT

This paper describes the experience gained by AREVA/COGEMA in 20 years of deconversion of depleted UF₆ at its Pierrelatte defluorination plant. With respect to this activity, AREVA/COGEMA has developed an extensive knowledge on issues such as optimised operating costs, preventive maintenance, health, environmental impact and has achieved a unique solution to store U₃O₈ on the long term and to recover and value as HF the fluorine component of depleted UF₆.

INTRODUCTION

The uranium enrichment industry generates large quantities of depleted uranium hexafluoride dUF₆ as a by-product. French national safety authorities have ever considered the chemical hazard associated with fluorine not to be acceptable for long term storage. They have required COGEMA to deconvert dUF₆ into a stable, fluorine free compound. Accordingly COGEMA has conducted defluorination operations as an extension of the enrichment industry since the industry began. The decision to industrialize a deconversion process was concomitant with the beginning of construction of the EURODIF enrichment facility.

Studies to deconvert dUF₆ 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.

Oxide product preferred for its stability, low solubility in water and low corrosiveness is sesquioxide U₃O₈, close to the pure chemical form of the uranium form of pitchblende, a prevailing form in the ore.

The fluorine content is recovered in the form of marketable 70% aqueous hydrofluoric acid.

Industrial feasibility was demonstrated for five years on a full-scale pilot plant. Main parameters such as resistance of process materials to UF₆ corrosion, filtration and scrubber column efficiencies, HF recovery, U₃O₈ compaction and collection, were tested and optimised.

In 1984, upon completion of the five-year pilot test program AREVA/COGEMA placed a first deconversion unit in service, so called W1. In 1993 a second unit, W2, came on line to double

the capacity. Development of the W2 process included design improvements based on the lessons learned from 10 years of operations.

The full COGEMA plant today allows to process 20,000 metric tons of dUF_6 per year, yielding roughly 17,000 mt of U_3O_8 and 10,000 Mt of 70% hydrofluoric acid per year. W1 plant has been successfully converting dUF_6 and operating commercially for more than 20 years, W2 for more than 10 years.

A major milestone will be reached in 2005: the total quantity of depleted UF_6 deconverted by the W plant will reach 300 000 Mtons.

W PROCESS

The aim is to convert through a dry process the hazardous UF_6 into the stable and durable U_3O_8 and a valuable co-product, hydrofluoric acid;

The UF_6 is first turned into vapor using wet steam autoclaves. Gaseous UF_6 reacts with overheated steam in the first part of the kiln. The hydrolysis exothermic reaction generates intermediate solid uranyl fluoride, UF_6 , and gaseous HF.

The solid UO_2F_2 falls into the second part of the kiln on a screw conveyor and reacts at a higher temperature with hydrogen and overheated steam. The endothermic pyrohydrolysis reaction produces the final oxide U_3O_8 , and hydrofluoric acid, which contains the excess of water needed for a fully completed conversion.

The U_3O_8 is continuously transferred, pneumatically transported to a compaction station before packaging, and then stored into dedicated warehouse.

Hydrogen fluoride mixed with steam leaves the reactor through a filtration chamber to remove any Uranium oxide from the gas; then the gases are condensed and scrubbed in such a way that an aqueous 70% HF is obtained. After monitoring, the HF is pumped to the HF storage area, pending transfer to road or rail tanks for sale and final shipment to customers.

The W plant features:

- a vaporization building with twelve vaporization autoclaves, distributed three per line of deconversion, leading to the continuous production of gaseous UF_6 ,
- four lines of deconversion, each consisting of a defluorination kiln with an annual throughput of 5000 MT of UF_6 , primary and secondary filtration devices, super heaters for steam, condensers for HF, air transportation of U_3O_8 powder and others connecting devices,
- One U_3O_8 compacting and conditioning station collecting the U_3O_8 powder coming from the four lines of deconversion. The U_3O_8 powder is packaged in 3 m³ containers specially design by COGEMA, so called DV70, containing an average of 10 MT of U_3O_8 ,
- one HF treatment unit consisting of intermediate tanks collecting the 70% HF coming from the four lines of deconversion, and the scrubber column
- a storage HF area consisting of twelve 20 m³ tanks, allowing the storage of a weekly production of acid,

- a service building including steam production
- A building accommodating the central control system, central control room, offices for staff operating management and maintenance support.

ES&H

COGEMA's vision for environmental management is structured as following:

- Integrate ES&H in all levels of the organization,
- Reduce releases of all types into the environment to a level as low as reasonably achievable, and monitor their environmental impact,
- Integrate safety and environmental protection from the outset of installation design
- Ensure company-wide concern for progress in environmental protection,
- Keep employees aware of safety standards and encourages participation in making safety a priority,
- Maintain communications to familiarize the public with the safety and environmental protection measures implemented at the plant.

COGEMA has operated the W plant according to this the public highest ES&H standards throughout its 20 years deconversion operations.

Operational procedures at W plant mandate meticulous reporting of any incident or events to the safety/quality/environment management of the site and the regulatory authority.

The effectiveness of the W plant ES&H program is demonstrated by the non occurrence of events with consequence on environment or contamination of Personnel during the last years of deconversion operations. Equivalent to NEPA, The COGEMA Pierrelatte site where is located the W plant is involved in the ISO14000 environmental process.

- Effluent and waste

The only liquid effluent generated by the process is the condensate of the water steam used to heat the UF6 vaporization autoclaves. Under normal operating conditions, this effluent contains no uranium.

The following are also collected and released after analysis:

- o Condensate from defluorination building air conditioning coils
- o Solutions collected from the HF areas

Liquid effluent from maintenance consists of effluent from washing/ decontamination of equipment components during maintenance. Annual average is less than 600 m³, uranium content less than 100 kg.

The release limits applicable for Gaseous effluent to W at the process scrubber are

- o Radioactivity less then 0.20 Bq/m³
- o HF less than 5mg/m³ and less than 1g per metric ton d'U₃O₈

Routinely the W releases are more than 10 times less than the limit applicable.

Waste identified as operating waste consists mostly of gloves and vinyl without significant concentration. Annual average solid waste from maintenance is less than 700 drums containing after decontamination less than 25 kg of uranium.

- Safety, security

In addition, the W plant has never had any significant accident or fatalities throughout its operations. Any incidents, like its causes, its effects and measurements taken to avoid the renewal of it are consigned chronologically on a register Hereafter are examples of main problems encountered and corrective actions taken:

- Escape of hydrogen to the park H₂,

This incident led to the installation of an evaluation of sealing to the reception of the trailers and the periodic control of the nuts carried out by the supplier.

- Loss of the electric power

This incident showed the good behaviour of the barriers of sealing and involved the modification of the connector block of the feeders of the electric station

- Escape HF in the THF area

This incident conducts to modify the rules of consignment.

The THF area was completely redesigned in 2002. Additionally all the acid effluent from the area is now cleanly collected and able to be injected in the HF co production

Maintenance

Preventive maintenance was established and adapted over the years in accordance with the continuously knowledge of equipment life expectancy.

Preventive maintenance is performed annually, during scheduled shutdown of individual process lines. The scheduled maintenance includes tests and repairs as well as change-out of equipment and parts. After removal the equipment and parts are checked, repaired when feasible, and stored until the next shutdown.

Additionally, a maintenance team allows performing any corrective maintenance to be needed on the day to day operating time.

Main improvements from 1984 till 2004

Lessons learned from operation of the W plant were continuously incorporated as improvements of the process technology over the years

Some examples are listed hereafter:

- On the defluorination kilns

- Optimisation of basic parameters such as shell thickness, shell alloy composition to reach a satisfactory technical and economical compromise with regard to the shell life time,

- Adjustment of the geometry of the injection nozzle for the UF_6 , steam and nitrogen to prevent clogging at the end of the nozzle and to ensure an instantaneous UF_6 hydrolysis inside the reaction chamber,
 - Adjustment of the stroke frequency of the hammer placed at the exit of the rotary kiln to prevent UO_2F_2 to stick on the walls of the kiln,
 - moving steam re-heaters closer to kiln to improve steam quality
 - Improvement access to kiln, motor and gearbox for maintenance activities
- On the gas process
- Development through a close collaboration between COGEMA and the manufacturer of a design for the condensers specifically for the W technology requirements
- On the U_3O_8 collection
- Development of U_3O_8 pneumatic transfer system to improve powder containment,
 - Increased the performance of the U_3O_8 compactor. The performance has been increased by a factor of 40% over the years
 - Automatization of U_3O_8 product packaging to reduce worker exposure
- On the HF filters and HF collection
- Allowed the integration of a systematic monitoring of filters plugging for optimising the counter –current unplugging cycle to increase the lifetime of the filters

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.

Beneficial Reuse

- U_3O_8

A today reuse of the depleted oxide is the mixed oxide Pu-U. This reuse covers only a very few part of the total annual quantity of depleted oxide.

One of the most promising reuse is the radiation shielding from x-rays or gamma rays for radiation protection

At that time, AREVA/COGEMA uses roughly 50 000 t of dU_3O_8 in DV70 to surround a storage of reprocessed Uranium oxide in Pierrelatte.

Reuse alternatives such as the chemistry of uranium based catalyst, uranium semiconductor properties and others were not investigated.

- HF

Clean hydrofluoric acid (70% aqueous HF) is produced in the deconversion process, thanks to a patented filtration system for off-gases from the rotary kiln.

All HF produced in the W plant meet all product specification and is sold in bulk to chemical companies in Europe. The co product HF enjoys a significant 30% of the European aqueous HF market.

In addition AREVA/COGEMA did a lot of survey with regards to the reuse of HF:

- From 70% HF to anhydrous HF.
Various alternatives were investigated.
 - o Distil the aqueous HF to obtain anhydrous HF and recycle the remaining azeotrope by re-injection in the defluorination kiln. This alternative was discarded since it required sensitive kiln technology and was more corrosive,
 - o distil the aqueous HF to obtain anhydrous HF and dry the azeotrope
 - Using NaF
 - Using solvent extraction
 - Using membrane electrolyser plus a distillation column
 - Using others process
- reuse the aqueous 70%HF by re injection in UF₄ conversion kilns,
- Produce a very high level purity HF to reach the electronic market.

Feasibility of some of these alternatives were demonstrated on a pilot scale or more, notably solvent extraction for anhydrous HF, reinjection of 70%aqueous HF in UF₄ kilns, and production of very high purity level aqueous HF.

Because of the current significant demand on the 70% HF, none of these alternatives has been yet considered opportune with regards to their profitability.

CONCLUSION

More than twenty years ago, it was quite a challenge for COGEMA to start defluorinating huge quantities of dUF₆, also considering it was an extra cost for the enrichment facility.

In twenty years and 300 000 t of dUF₆ defluorinated, COGEMA has won its challenge and has achieved a unique way to safely manage dUF₆. COGEMA has constantly improved its technology, so as to make it even safer and cost effective, allowing other enrichment companies to take benefit of this unique experience