Nuclear Liquid Wastes Calcination: The High-Level French Experience – 17184

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ABSTRACT

Calcination is an efficient process for volume reduction and stabilization of nuclear liquid wastes. It is often the first step of waste containment processes such as vitrification or grouting.

The CEA (French Alternative Energies and Atomic Energy Commission) and AREVA have acquired a high-level experience in the field of calcination through more than forty years of R&D and industrial operation. During this period, a broad range of liquid wastes have been studied and treated.

R&D work and associated engineering studies allowed defining the design and sizing of the equipment and the process control parameters to be applied for the calcination of all kinds of solutions.

The calcination process has been qualified for the following effluents amongst others:

- Liquid waste from UOx fuel reprocessing
- Liquid waste from UMo fuel reprocessing (high molybdenum and phosphorus contents)
- Hanford HLW
- Liquid waste from D&D operation (sodium bearing waste)

This paper presents several studies led by the Joint Vitrification Laboratory (L.C.V), a common research laboratory between CEA and AREVA in charge of qualifying new processes and matrices for waste containment. These studies allowed defining the calcination rules, in particular for very hard to process solutions such as effluents with high boron, molybdenum and sodium contents.

The feedback from industrial operation of the calcination process with fission products and effluents from D&D operations, highly loaded with sodium, is also presented.

INTRODUCTION

Calcination is an efficient process for volume reduction and stabilization of nuclear liquid wastes. It is often the first step of liquid waste immobilization processes such as vitrification or grouting.

The CEA (French Alternative Energies and Atomic Energy Commission) and AREVA have acquired a high-level experience in the field of calcination through more than forty years of R&D and industrial operation. During this period, a broad range of liquid wastes have been studied and treated.

In France, the R&D on thermal processes for waste containment is led by the Joint Vitrification Laboratory (LCV). The LCV is a common research laboratory, between CEA and AREVA, in charge of qualifying new processes and matrices for waste containment. In this context, the LCV has a large range of calcination pilots, from laboratory scale to industrial scale, and has developed a methodology for the qualification of treatment of active solutions by calcination process.

R&D work and associated engineering studies allowed defining the design and sizing of the equipment and the process control parameters to be applied for the calcination of all kinds of solutions. R&D studies also allowed getting a refined insight into calcination mechanisms and defining the calcination rules, in particular for very hard to process solutions such as effluents with high boron, molybdenum or sodium contents.

The calcination process has been qualified or pre-qualified for the following effluents amongst others:

- Liquid waste from UOx fuel reprocessing.
- Liquid waste from UMo fuel reprocessing (high molybdenum and phosphorus contents).
- Liquid waste from D&D operation (sodium bearing waste).
- Hanford HLW.
- Liquid waste from West Valley.

This paper presents the R&D and qualification work, in the field of calcination process, led by the LCV and the feedback from engineering studies such as modeling.

The feedback from industrial operation of the calcination process with fission products and effluents from D&D operations, highly loaded with sodium, is also presented.

CALCINATION PROCESS DESCRIPTION

The functions required from a calciner for liquid waste treatment are presented below:

- Evaporating and drying the liquid feed,
- Decomposing the salts contained in the solution,
- Producing a calcine with the required physical and chemical characteristics (particles size, water/NOx content, …).

The design of the calciners qualified at the LCV includes:

- An electrically heated cylindrical furnace equipped with 8 half-shells constituting 4 zones in the length of the calciner. These half-shells include

heating resistance to heat the tube through radiative transfer, thermal insulation and thermocouples,
- a rotating tube,
- rollers bearing that support the rotating tube,
- an upper end-fitting ensuring leak-tightness at the rotating tube upper end, with connections for off-gas exhaust and for supplying the liquid feeds,
- a lower end-fitting ensuring leak-tightness at the rotating tube lower end and guiding the calcine into a specific canister or into a melter,
- a tube motor drive unit.

The tube is equipped with a rabble bar for calcine mixing and size calibration and with a screen for limiting maximum size of calcine particles sent downstream.

The calciner is controlled by assigning heating temperature set points to the electrical resistors. The calcining performance is observed by monitoring the heating power variations. Other process parameters such as tube expansion and tube temperatures can also be monitored.

Additives can be added prior to calcination in order to avoid sticking issue in the tube, in particular for solutions highly loaded with sodium.

Sugar can also be added to the feed prior to calcination in order to reduce some of the nitrates and to limit ruthenium volatility.

In France, calcination is used in a two-step vitrification process for highly active solutions treatment. In this configuration, the calcine falls directly into the melter along with the glass frit which is fed separately.

An off-gas treatment system is connected at the upper end-fitting. The off-gas treatment unit purifies the gas streams before stack release and can recycle particulate material into the process.

The off-gas treatment unit is sized according to the feed solution characteristics and the flow rate.

Depending on the solution to be treated, the off-gas treatment system (OGTS) can be composed of a dust scrubber, a water and nitric acid vapor condenser, an absorption column, a washing column, a ruthenium filter, and HEPA filters. The most active gas washing solutions can be recycled from the wet scrubber to the calciner. Off-gas treatment must be capable of ensuring a satisfactory decontamination factor in the gas exhausted from the calcining operations.

The calciner and OGTS currently operated at La Hague plant for the treatment of fission products coming from ongoing reprocessing activities and for the treatment of solutions highly loaded with sodium or molybdenum is shown schematically in Figure 1.

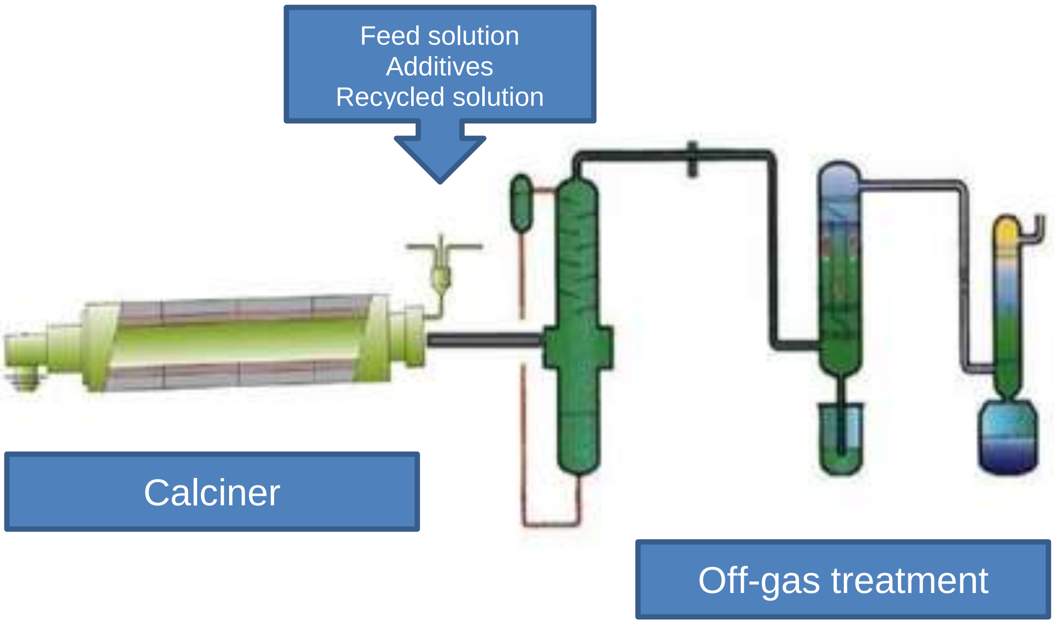

Fig. 1. Calcination process operated at La Hague plant

R&D AND QUALIFICATION

Qualification methodology

Qualification of a solution for processing by calcination involves all the necessary steps to define the following elements:

- nature and type of the additives required to obtain a satisfactory calcine,
- solution adjustment parameters (additives quantity according to the composition of the solution to be processed),
- calcination parameters to be applied according to the feed rate (heating power, rotating tube speed, …),
- calcination parameters to be applied during transient modes,
- maximum production capacity with respect to the design and sizing of the industrial equipment.

The qualification methodology is based on a succession of experimental procedures on tools ranging from bench scale to industrial scale, in order to ensure complete industrialization.

Calcine quality is characterized by the following measurements:

- particles size distribution,
- density,
- chemical composition,
- NOx content,
- extent of calcination.

A proper calcine is distributed according to a normal law with low range. The majority of the nitrate salts present in the solution have to be decomposed. Calcine has to be chemically homogeneous.

R&D tools available at the LCV

R&D tools available at the LCV are shown in Figure 2. These tools provide the whole range of results necessary to explore, develop, and optimize calcination operations for the rotary tube process.

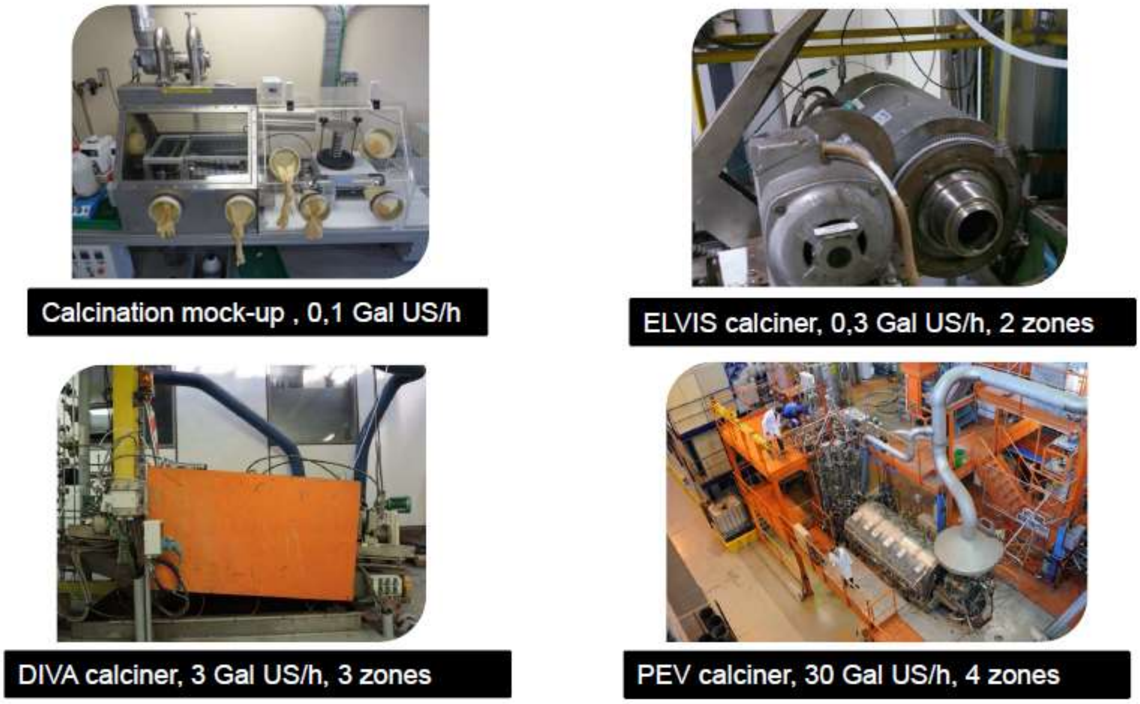

Fig. 2. Calciners available at the LCV

<u>Calcination mock-up and ELVIS calciner:</u>

The calcination mock-up and ELVIS calciner treatment capacity are respectively 0,1 Gal US/h et 0,3 Gal US/h.

The calcination mock-up has only one heating zone. ELVIS calciner has two heating zones.

The calcination mock-up and the ELVIS prototype are dedicated to basic studies related to the impact of different additives on the calcination for a given solution. The calcination mock-up is fit with a window allowing viewing of the flow and thus the determination of potential flow and retention issues in the tube.

The small scale of these pilots allows performing parametric studies such as Design of Experiments. Results from tests on these prototypes are used to develop simulation tools for complete description of physical and chemical phenomena in the process.

Moreover, these small scale tools enable to optimize of the full scale pilot design, and to restrict the number of full scale tests to the minimum.

<u>DIVA calciner:</u>

The DIVA pilot is a 1/10 scale equipment. The treatment capacity is 3 Gal US/h, the calciner has three heating zones.

This pilot allows validating the calcination additives and implementing parametric studies in order to determine the following settings for the industrial process in order to ensure the correct calcine quality and flow:

- amount of additives to feed into the process according to the feed solution composition,
- heating parameters,
- rotating tube speed.

PEV calciner:

The PEV calciner is an industrial-scale pilot included into a full mock-up of the La Hague vitrification lines. Its maximal treatment capacity is around 30 Gal US/h.

The PEV calciner has 4 heating zones.

The PEV full scale calciner allows performing the last step of qualification prior to industrial implementation:

- defining the industrial treatment capacities,
- defining and validating the process control parameters to be applied for nominal operation at industrial capacity (heating power, rotation speed, …),
- defining and validating the process control parameters to be applied for transient modes,
- Optimizing the process control parameters.

Tests performed on the PEV calciner can be decomposed as follows:

- Nominal conditions tests for defining the nominal parameter values which guarantee that the industrial-scale calcine has the proper characteristics.
- Sensitivity tests for validating an operating range for operating parameters over the entire expected feed composition domain, to maintain the nominal throughput.
- Transient modes tests for defining the operating parameters adjustments necessary to guarantee the proper characteristics of the calcine and to avoid detrimental effects during transient phases.

Process qualifications synthesis

The calcination process has been qualified or pre-qualified at the LCV for the following effluents (non-exhaustive list):

- Liquid waste from UOx fuel reprocessing
- Liquid waste from UMo fuel reprocessing
- Liquid waste from D&D operation
- Hanford HLW
- Liquid waste from West Valley

The noteworthy elements are presented hereafter:

Liquid waste from UOx fuel reprocessing:

Calcination of UOx fission products, from ongoing reprocessing activities, has been qualified at the LCV in the ‘80s.

The process control parameters and the adjustment parameters (calcination rules) have been defined for nominal operation and transient modes. They allow producing a satisfactory calcine and avoiding clogging issues in the tube. The maximal qualified treatment capacity is around 30 Gal US/h.

Aluminum nitrate is added prior to calcination to avoid sticking issue in the calciner due to the melting of $NaNO_3$. Sugar is also added to the feed prior to calcination to reduce some of the nitrates and to limit ruthenium volatility. A huge amount of these solutions has been calcined since the industrial commissioning of La Hague plant. The feedback is presented later in the paper.

Liquid waste from UMo fuel reprocessing:

UMo solutions (fission products from UMo spent fuel reprocessing) are very hard to process because of the high molybdenum and phosphorus contents. The main features of the waste behavior in the process are the following:

- The solutions have a strong tendency to stick in the calciner.
- Calcining exhaust stream may cause strong clogging issues in off-gas treatment equipment.

The calcining parameters (heating power and rotation speed) have been defined by specific tests for various throughputs. The feed solution composition adjustment has also been defined during the inactive qualification. Compliance with calcining and solution adjustment parameters ensures that a proper calcine is obtained and prevents sticking issues in the tube.

Specific devices, at the outlet of the calciner, were also defined and qualified to limit the sticking of molybdenum salts from calcining exhaust stream in off-gas treatment equipment.

A large amount of these solutions has been calcined at La Hague plant since 2013. The feedback is presented later in the paper.

Liquid waste from D&D operations:

D&D solutions (corrosive solutions from decommissioning and dismantling of the UP2-400 facility at La Hague plant) are highly loaded with sodium and boron. These solutions are very hard to process; the main features of the waste behavior in the process without solution adjustment are detailed hereafter:

- Formation of a sticking sludge (which can clog on the rabble bar).
- Crystallization and formation of a solid ring which can lead to full clogging of the tube.
- Sticking of molybdenum.

The figure 3 shows calcine from surrogate D&D solution, highly loaded with sodium, obtained without applying the appropriate adjustment and operating parameters (photograph taken inside the tube). The calcine obtained is erratic and oversize; Clogging and sticking phenomena are also observed in the tube.

Fig. 3. Calcine obtained without applying the appropriate adjustment and operating parameters

Specific additives have been studied and selected according to the specific issues presented above. Calcination rules have been defined and patented in order to avoid clogging and sticking issues and to obtain a proper calcine distributed according to a normal law with small range.

Figure 4 shows calcine from surrogate D&D solution, highly loaded with sodium, obtained with the appropriate solution adjustment and operating parameters.

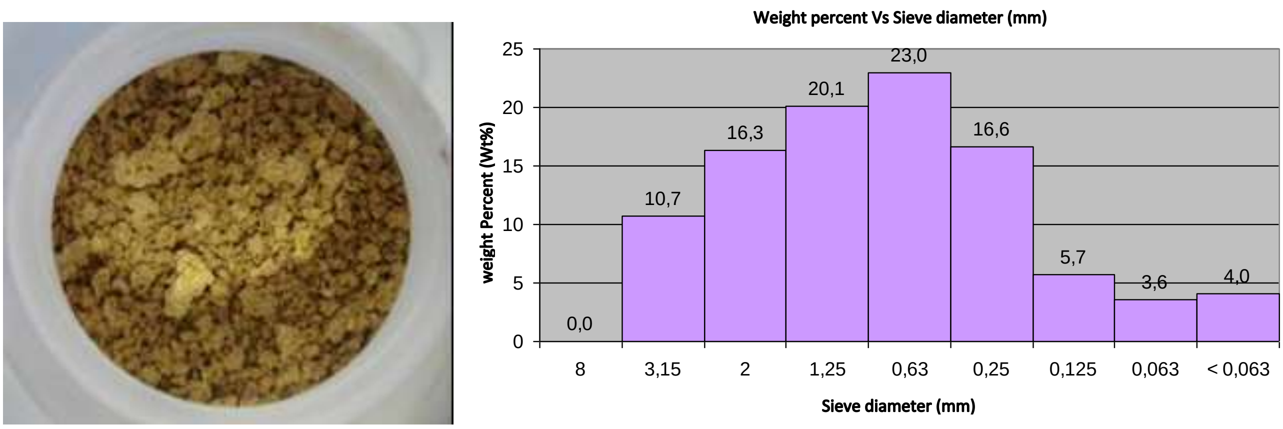

Fig. 4. Calcine obtained with the appropriate adjustment and operating parameters

Operating and solution adjustment parameters defined by the R&D teams ensure that a proper calcine is obtained and prevents sticking and clogging issues in the tube. The calcine size is distributed according to a normal law with small range. Majority of the salts present in the solution have been decomposed.

A large amount of these solutions has been calcined at La Hague plant since 2010. The feedback is presented later in the paper.

<u>Hanford HLW:</u>

Feasibility tests for Hanford solutions calcination were performed at the LCV. Hanford solutions studied are C106 effluent (basic solution loaded with suspended matter) and AZ-BLEND solutions (tanks AZ101 and AZ102). The tests performed demonstrated the feasibility of calcining C106 solution and AZ-BLEND solutions after adjustment.

Operating parameters such as heating power and rotating tube speed have been determined; solution adjustment parameters such as sugar content have also been determined.

The tests performed allowed a satisfactory calcine production. The process control parameters applied also allowed avoiding sticking and clogging issues in the tube. The process treatment capacity achieved was around 11 Gal US/h.

Liquid waste from West Valley:

Feasibility tests for West Valley solutions calcination were performed at the LCV. The solution studied was a mix of $8D_2$ tank and $8D_4$ tank.

The tests performed demonstrated the feasibility of calcining the West Valley solution. The calcine obtained was satisfactory.

The amount of aluminum and sugar to be added for a suitable calcination has been determined. The process control parameters applied also allowed avoiding sticking and clogging issues in the tube. The process treatment capacity achieved was around 11 Gal US/h.

Basic phenomena understanding

General points:

Many studies dedicated to basic phenomena understanding in the calcination process have been carried out at the LCV. The tests, carried out at laboratory scale, allow understanding chemical phenomena and thus selecting the proper additives to be added in order to obtain satisfactory calcines and to avoid sticking issues in the tube.

Many studies have been in particular performed in order to understand and to address the sticking phenomena of the sodium in the process.

The main results related to $NaNo_3$ behavior in the calcination process are presented hereafter.

Main results related to $NaNO_3$ behavior in the calcination process:

Two simplified $Al(NO_3)_3{\cdot}9H_2O$ - $NaNO_3$ calcines, with variable proportions of $Al(NO_3)_3{\cdot}9H_2O$ and $NaNO_3$, have been studied in order to understand the sticking behavior of sodium in the calcination process. These calcines, presented in table 1, were carried out by processing the corresponding nitric acid solutions in ELVIS calciner.

TABLE I. Oxide composition of calcine samples (wt%)

	Wt% Na_2O	***Wt% Al_2O_3***	***$[Na_2O]$ /$[Al_2O_3]$+$[Na_2O]$ ratio***
$NaNO_3$	*100*	*0*	*0*
Calcine 1	*20*	*80*	*0,2*
Calcine 2	*50*	*50*	*0,5*

The morphology and microstructure changes of these simplified calcines, with variable amount of sodium, were identified by environmental scanning electron microscopy (ESEM) and X-EDS analyses (Bruker 5010 EDS).

The images reported in figure 5 show a mixing of powder constituted by sodium nitrate (grey color) and aluminum oxide (white color). Calcine 2, photographed at 100 °C, shows a phase which seems to be a frozen liquid and a phase that looks rather porous. The calcine reactions monitored at High-temperature (heating at 400°C at a rate of 20°C/min with a pressure of 350Pa) illustrated the strong difference between calcine 1 and calcine 2. Indeed, analyses of images highlight that calcine 2 (enriched in sodium) is melted at 400 °C while calcine 1, heated at 400 °C, remains solid.

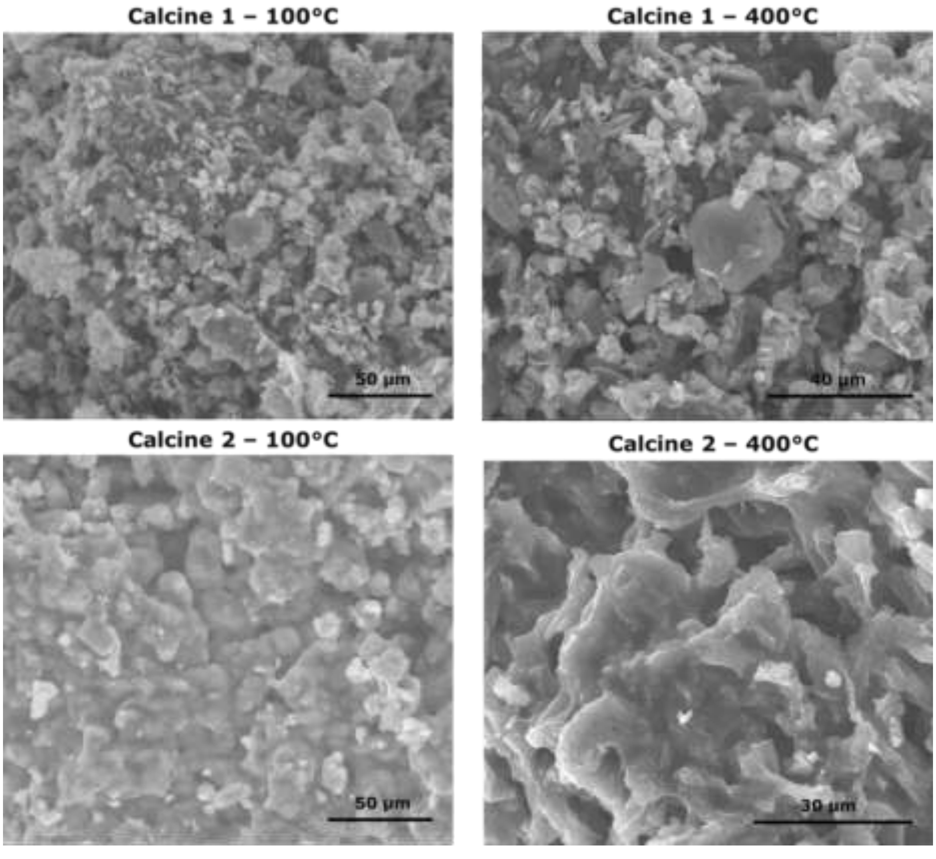

Fig. 5. Environmental SEM images of calcines 1 and 2 heated at 100°C and 400°C

XRD analysis at ambient temperature was carried out on ground samples of calcines 1 and 2, to determine the mineralogy of the compounds (figure 6). The calcine diffractograms reveal a single crystalline phase corresponding to hexagonal

$NaNO_3$ (figure 6). No peaks can be assigned to Al_2O_3. This observation is due to the presence of Al_2O_3 amorphous phase [1].

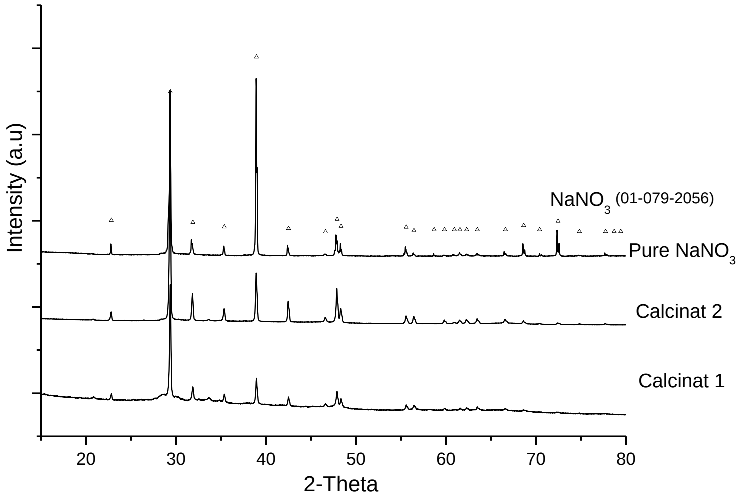

Fig. 6. X-ray diffraction diagrams of calcines 1, 2 and $NaNO_3$

Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) measurements performed (argon atmosphere in platinum crucibles, rampe 10°C·min^{-1} up to 1300°C) on calcine samples reveal the presence of two principal endothermic peaks (figure 7). The first one, occurring just above 300°C, is not associated with a loss of mass, and can be assigned to melting of residual $NaNO_3$.

The second, broad and complex, observed between 600 and 900°C is accompanied by mass loss and corresponds to the decomposition of the remaining nitrates.

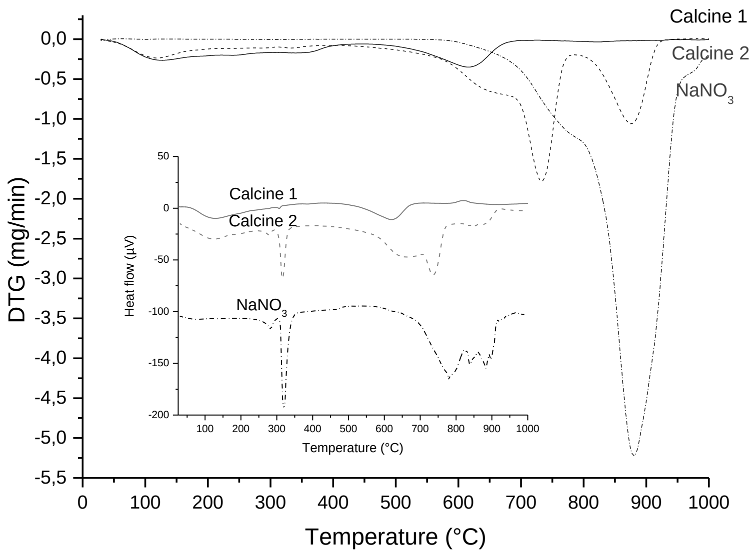

Fig. 7. Differential thermal and thermogravimetric analyses of calcine samples and $NaNO_3$ pure phase

The absence of thermal peak just above 300 °C for calcine 1 highlights that there is no melting of $NaNO_3$. This is due to the low quantity of sodium nitrate and the integration of this compound in the amorphous alumina matrix.

This study allows understanding the sticking behavior of sodium nitrate in the calciner. Indeed, the melting temperature of $NaNO_3$ (just above 300 °C) corresponds to operating temperatures in the tube. The presence of solid aluminum oxide, formed at lower temperature, enables to avoid sticking issues in the tube.

ENGINEERING STUDIES

Design and sizing

AREVA calciners are developed with a modular and removable design. In this way, all the calciner parts are remotely-dismountable and can be separately replaced (heating zones, rotating tube, upper end-fitting, lower end-fitting, gaskets,…).

The remotely-removable design defined by the engineering teams, augmented by the high knowledge and experience of the La Hague operators allows some high level maintenance operations and thus increasing the overall efficiency of the calcination process operated at La Hague plant.

Many design improvements have also been led by AREVA PROJECTS (former SGN), with close collaborations of the R&D teams, in order to improve the reliability of the calciner process operated at La Hague plant.

The main improvements are presented hereafter (non-exhaustive list):

- Change in the design of the heating elements.
- Maintainability improvements for the tube.
- Rubble bar improvements.

Modeling

A calciner model has been developed by the engineering teams in order to improve process knowledge [2]. The code is used to solve the equations governing the following main phenomena:

- Liquid flow all along the tube (driven by gravity).
- Liquid evaporation.
- Solution denitration and reduction reactions (38 reactions taken into account).
- Half-shell power supply.
- Tube expansion.
- Heat transfers.
- Rotation.

This model was qualified for UOx fission products feeding and water feeding by comparing its results with measures performed on the PEV calciner.

The comparison between the experimental and model results is very satisfactory as illustrated by figure 8 (water feed and surrogate UOx fission products feed).

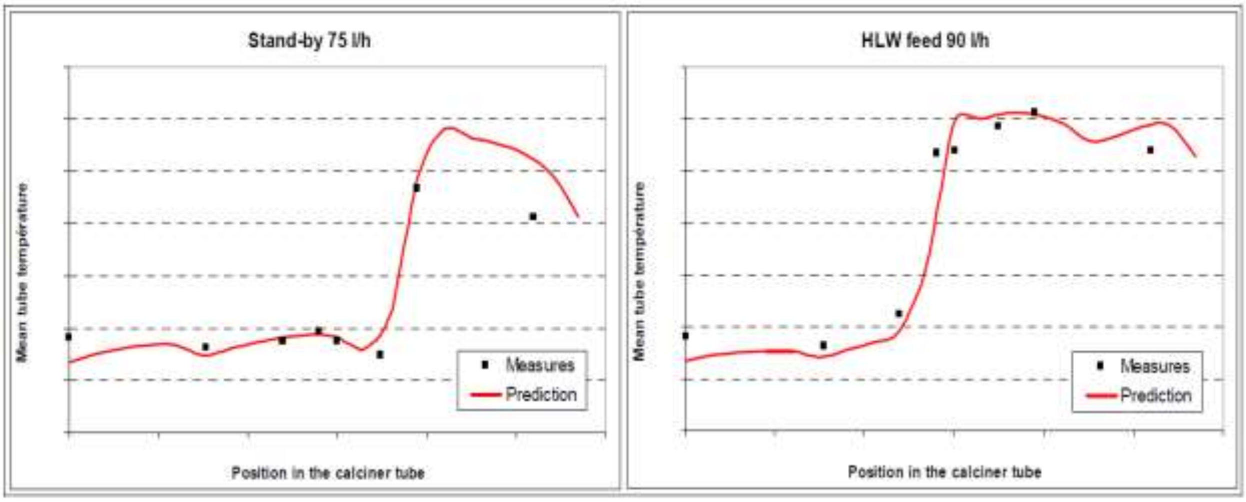

Fig. 8. Comparison of measured and predicted tube temperatures

This model is a useful tool for development and optimization of operation. For instance, it is possible to determine temperature profiles in the tube according to the operating parameters (feed rate, set-point temperature, heating power, …) and/or several design parameters (insulating material and dimension of the cylindrical heating zones, thermocouple positions, maximum allowable power, tube thickness, …).

The model also allows determining, for a given configuration, what would be the maximum throughput. It is also feasible to determine the temperature profiles in various configurations for capacities close to the highest achievable throughput. This model was a determining tool in planning and achieving throughput increases for the La Hague calciners [3].

The model developed by AP, coupled to the LCV expertise, allows explaining the influence of operating parameters and figuring out the phenomena in the process. In fine, these works allow optimizing the operating modes and improving process performance.

FEEDBACK FROM INDUSTRIAL OPERATION

Highly active solutions processing (calcination and vitrification) at La Hague plant started in 1989 and is currently ongoing. Highly active solutions processing (calcination and vitrification) at Marcoule plant ran from 1978 to 2012.

The amounts of solutions treated are presented in the table hereafter (as of November 8, 2016).

TABLE II. Amounts of solutions treated at La Hague and Marcoule plants

La Hague Plant			**Marcoule Plant**
UOx fission products (m^3)	**UMo fission products (m^3)**	**D&D solutions (m^3)**	**fission products from gas cooled reactor fuel reprocessing (m^3)**
20259	130	313	2870

For the three types of active solutions, compliance with solution adjustment parameters and process parameters, defined during the R&D phase, allowed producing satisfactory calcines and prevented sticking and clogging issues in the tube, even for very hard to process UMo fission products (highly loaded with molybdenum) and D&D solutions (highly loaded with sodium and boron).

Even if some difficulties occurred, operation teams experience along with engineering and R&D support allowed managing them.

Since the start-up of calcination operations at La Hague plant, the design of the calciner has been greatly improved to allow easier and quicker maintenance and to considerably increase its lifetime: calciner tubes can now last for more than 45,000 hours of operation. As for many pieces of equipment in the La Hague facilities, the implemented improvements deal not only with design and maintainability, but also, through a continuous knowledge effort, with optimization of operation. Those two aspects are closely related and, together, have resulted in a considerable enhancement of operation records over the years.

CONCLUSION

Calcination is an efficient process for volume reduction and stabilization of nuclear liquid wastes.

The CEA and AREVA have acquired a high-level of experience in the field of calcination through more than forty years of R&D and industrial operation. During this period, a broad range of liquid wastes have been studied by the R&D teams and a huge amount of solutions have been treated by the industrial operator (more than 20700 m^3 at La Hague plant and 2870 m^3 at Marcoule plant).

Compliance with solution adjustment parameters and process parameters, defined by the R&D teams, allowed producing satisfactory calcines and prevented sticking and clogging issues in the tube, even for very hard to process UMo fission products (highly loaded with molybdenum) and D&D solutions (highly loaded with sodium and boron).

R&D tools available at the LCV allow full qualification of the calcination process (process parameters definition, calcination rules definition, …). They also allow basic studies implementation; in particular they enabled to understand chemical phenomena in the calciner such as sticking behavior of sodium nitrate.

Many design improvements have been led by the engineering teams, with close collaborations of the R&D teams, in order to improve the reliability and the performances of the calciner process operated at La Hague plant.

A calciner model has also been developed in order to improve process knowledge. This model allows optimizing the operating modes and improving process performance.

The continuous improvement policy implemented in AREVA facilities, in the field of design, maintainability and process knowledge, coupled with the close collaboration between R&D teams, engineering teams and the industrial operator, have led to a considerable enhancement of operation records and to a high mastery and knowledge of the calcination process.

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