

THE FRENCH EXPERIENCE IN DRY MILLING OF NUCLEAR CERAMIC POWDERS

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ABSTRACT

Dry milling is a keypoint process step in the manufacturing of nuclear ceramics, either for plutonium recycling in MOX fuel or for its immobilization by ceramification. In both cases, dry milling provides the sufficient level of micronization and micro-homogeneity necessary for a complete reactive sintering.

The selection of the best technical and cost effective technology for dry milling of nuclear powders must consider the stringent process requirements and the specific constraints due to nuclear environment. Moreover, a wide testing program is necessary to validate the choice.

The huge experience of COGEMA in dry milling, gained through the development and industrialization of MOX manufacturing processes clearly show that ball milling fits perfectly well on an industrial scale both process and technological requirements of the function: high quality product, high reliability and maintainability of the equipment, and facility of operation.

INTRODUCTION

In France, the manufacturing of MOX fuel for recycling of plutonium is now a mature industry, illustrated by the MELOX plant that has now reached its nominal capacity. In USA, moxidification and ceramification are the solutions that have been retained for recycling or immobilizing the excess of plutonium. The two processes, moxidification and ceramification have in common the manufacturing of a technical nuclear ceramic with very stringent specifications. In particular, both processes require a very fine milling of nuclear oxides. This milling step is a keypoint process step that governs the quality of the final product.

THE ROLE OF MILLING IN NUCLEAR CERAMICS MANUFACTURING PROCESSES

Fundamentals

Technical ceramics, especially in nuclear industry, are characterized by very stringent specifications. In particular, the ceramic must present an accurate composition, defined by the crystalline phase equilibrium or the formation of a specific solid solution. The role of the

ceramic manufacturing process is to turn from individual components (generally metallic oxides) to the desired final composition.

In nuclear industry, specific constraints like criticality and safety or the nature of inlet products have led to develop dry processes for ceramic manufacturing. The most commonly used processes are based on a reactive sintering of a compact, obtained by cold pressing of a mix of powders. The formation of the desired ceramic is then obtained through diffusion mechanisms during the sintering step, at the same time as densification of the ceramic.

For given elements, the diffusion phenomena are governed by thermodynamical conditions (temperature, sintering atmosphere). However, a technological constraint limits the possibility of acting on these parameters to enhance the diffusion coefficients (for example: oxidizing atmosphere leads to higher diffusion coefficients but requires specific furnace technologies). So, interdiffusion distances remain relatively low (typically a few microns), which is most of the time not enough to provide a complete reaction when considering the initial granulometry of inlet products.

The best way to obtain a complete reaction during the sintering step is to provide a sufficient micronization and micro-homogeneity of powders in the green compact. The role of the milling function in dry ceramic manufacturing processes is to achieve these micronization and micro-homogeneity. So, it is a keypoint process step that determines the quality of the final product.

Nuclear ceramic manufacturing processes

Uranium/Plutonium fuel manufacturing represents the widest industrial experience in nuclear ceramic elaboration by reactive sintering. It includes U/Pu fuel manufacturing for fast breeder reactors and MOX fuel manufacturing for light water reactors.

Remark:

We do not consider here uranium fuel manufacturing processes, which do not requires reactive sintering (monocomponent ceramic).

In U/Pu fuel manufacturing processes, especially for MOX fuel, plutonium must form with uranium a solid solution $(U,Pu)O_2$. From the quality of this solid solution formation depends the good behavior of the fuel in reactor and the good solubility of the fuel in further reprocessing operations.

In France, FBR fuel manufacturing is based on the COCA (CO-milling CAdarache) process, and MOX fuel manufacturing is based on the MIMAS (MIcronization MASTer blend) and the A-MIMAS (Advanced-MIMAS [3]) processes (figure 1).

In the COCA process, uranium and plutonium oxides are micronized and homogenized together in a milling apparatus, before pressing and sintering. Specification on solubility is therefore less stringent than in MOX fuel, because of higher burnups of FBR fuels, which lead to more soluble irradiated ceramic.

In the MIMAS process, a master blend of micronized and homogenized UO_2 and PuO_2 is first realized by milling, then diluted to the final Pu content by uranium oxide. Contrary to the master blend, this dilution does not require a micronization of powders (only a homogeneous blending), so a conventional blender is used.

In both processes, dry ball mill is used to provide micronization and micro-homogeneity. This experience is detailed later in the paper.

Another example of nuclear ceramic manufacturing is the future ceramification for immobilization of plutonium in excess in the United States. As presented last year in Tucson [1], the process under consideration is similar to MOX fuel manufacturing processes, including a milling step of actinide oxides, a blending step with the ceramic precursors, a pressing step and a reactive sintering step (figure 2). The role of the process is to form specific crystalline phases, which have been selected for their good properties of actinide incorporation and long term behavior.

As for U/Pu fuel manufacturing, the milling step has to provide a sufficient micronization of the actinide powders to avoid the presence of non reacted particles after sintering.

IMPORTANCE OF TECHNOLOGICAL CHOICES

Process/Technology interdependency in powders processes

In the previous paragraph, we have defined the functions of the milling step in nuclear ceramic manufacturing processes: micronization and micro-homogenization. We must now consider the selection of the technology to achieve these functions.

In powders processes, this selection is of primary importance because it exists a strong interdependency between process and technology. In others words, in a process step, the characteristics of the outlet powder is highly dependent on the technology that has been used.

In milling operation, different mechanisms can lead to the fragmentation of particles:

- compression,
- shearing,
- attrition,
- impact,

either due to grinding elements or due to impact between particles.

Moreover, fine and ultrafine dry milling of powders is characterized by two opposed processes: fragmentation and agglomeration. It means that, simultaneously to the fragmentation of particles occurs the formation of agglomerates whose level of cohesion can highly vary.

Finally, depending on the technology, continuous or not, "perfectly stirred tank reactor" type (like the ball mill) or not, a blending function can be achieved or not in the milling equipment.

So, each milling technology is characterized by its predominant fragmentation mechanisms, its own level of agglomeration and its own level of blending, that can also vary with the operating parameters of the equipment. As a result, for a same function (milling), the characteristics of the milled powder (granulometry, level of agglomeration, specific surface, density, flowability...) will be highly dependent on the technology that has been used.

As a consequence, the definition of the downstream process has to take into account the specific characteristics of the milled powder: necessity or not to add a blending step, a forced sieving step, transferability of the powder...

Specific constraints in nuclear applications

More than in any industrial field, reliability and maintainability of process equipment are of prime importance in the nuclear industry.

Specific constraints on equipment selection in nuclear powder processing, especially when plutonium is present, are due to the following requirements:

- containment requirements, needing to place process equipment in gloveboxes and to confine the radioactive materials as much as possible in the process equipment;
- radiation protection requirements, needing implementation of radiation shielding and minimization of personnel operation near gloveboxes;
- stringent requirements on the end-products, needing process equipment able to provide a highly constant quality and to have a very stable working point easy to adjust.

Meeting these specific constraints leads to select only equipment that have the following characteristics:

- high reliability in order to minimize needs for maintenance, and so, to minimize dose to the personnel due to maintenance operations;
- high maintainability in order to make easier and to minimize time duration of unavoidable maintenance operations;
- high cleanability, i.e. a design enabling to minimize the powder hold-up of the equipment in order to limit the mixing between successive lots of different characteristics (Pu content for instance) and to make easier maintenance operations;
- high robustness, i.e. an equipment able to provide a highly constant quality without needing an accurate and constant tuning.

So, both process implications and specific constraints show that the choice of a technology in a nuclear powder process must be highly considered. The validation of this choice must go through a complete program of testing before industrialization.

THE COGEMA APPROACH OF INDUSTRIAL DEVELOPMENT

Global approach

For any process function, after establishing detailed specifications including process and technological requirements, COGEMA uses different tools to select the best technical and cost effective technology:

- library of standard equipment,
- experience feedback from existing facilities,
- knowledge of state-of-the-art processes and technologies,
- research and development facilities.

This global approach, applied to the design of a new MOX facility, has been detailed in [2] from the conceptual to the detailed design. Let us just present here the testing approach which is applied in order to qualify a process equipment and in particular a milling equipment.

Testing approach

The testing approach to qualify a process equipment consists of three different phases, each with their specific objectives:

Laboratory tests with uranium:

These tests aims at evaluating the technology towards the requirements and to give a preliminary definition of operating parameters to obtain the required characteristics on the outlet products. They can be carried out with different surrogates of plutonium, depending on the physical characteristic that is to simulate.

They are very informative but not sufficient, neither on a process plan (because only tests with plutonium can definitively inform on the quality of end products: pellets...), nor on a technological plan (because small-scale tests are not sufficiently representative of industrial operation).

These tests can be carried out either through co-operation with research institutes like the French Atomic Energy Commission (CEA) or in centers owned by COGEMA like the COGEMA Advanced Development Center (CDA) near Grenoble in France.

Laboratory tests with plutonium:

These tests enables to validate the quality of sintered products towards the process requirements (phase composition, Pu distribution...). They are essential because no surrogate can completely simulate both physical (powder properties) and thermodynamical (diffusion phenomena) behavior of plutonium oxide.

These tests are preferentially performed in the CEA laboratories in case of new process development or at the MELOX laboratory test line in case of process evolution in the existing plants.

Industrial scale tests with uranium:

They aim at validating the process technologies in representative conditions.

On a process plan, they enable to evaluate scale effects, which can highly influence the results in powder processes. In case of milling for instance, industrial scale tests can show specific problems that have not been revealed by small scale tests: heterogeneous milling throughout the equipment due to the design of the equipment or the lack of blending function, need for a too accurate tuning of the equipment to obtain good outlet characteristics...

On a technological point of view, it is still more obvious: only industrial scale testing enables to evaluate operability, maintainability, cleanability of the equipment.

These tests are performed at the CDA that is equipped with medium or full-scale pilots for each process step of fuel manufacturing.

APPLICATION: THE BALL MILL IN MOX FUEL MANUFACTURING PROCESSES

The previous approach, applied to milling step in U/Pu fuel manufacturing led COGEMA to retain dry ball milling to fit both process and technological requirements of the function.

Description of dry ball milling

A ball mill is composed of a closed vessel (generally cylindrical), which can be set in rotation around its axis (horizontal or slightly inclined). Inside the vessels are introduced a load of grinding elements and a load of powder. Balls and powders have a free motion during the rotation of the tank.

Form, size and nature of the grinding elements are chosen in function of the requirements (in particular level of milling). In COGEMA MOX plants, they are made of an uranium alloy in order to minimize powder pollution due to erosion of grinding elements.

Depending on the level of rotation speed of the tank (compared to the critical speed corresponding to the centrifugation of the grinding elements), different cases must be distinguished, as illustrated in figure 3. In MOX processes, sliding and rolling over are the preferred working rates, leading to attrition and compression as predominant fragmentation mechanisms.

Once "geometrical" parameters have been fixed (characteristics of grinding elements, effective volume of the tank, rotation speed, angle of slope...), the working of a ball mill can be easily mastered through the control of a few parameters:

- J: grinding ball-filling ratio, defined as the ratio of apparent volume of grinding elements on effective volume of the tank;
- U: powder-grinding ball ratio defined as the ratio of apparent volume of powder on void volume between the grinding elements;
- K: load factor, defined as the ratio of grinding element mass on powder mass.

The knowledge of 2 of these 3 parameters and the milling duration are sufficient to master operating conditions.

Mains characteristics of dry ball milling

Due to the very simple design of the vessel, to the adjusted filling factor and to the free motion in the tank, ball milling provides an excellent mixing of the entire load of powder and an excellent homogeneity of milling. So, it fits perfectly well the process needs in MOX fuel manufacturing: not only a particle size reduction, but also a very homogeneous and fine distribution of plutonium oxide in uranium oxide.

When considering the evolution of powder characteristics during milling (granulometry and specific surface, see figure 4), one can explain the action of milling as a breaking action of the bridges that exist between elementary crystallites in the aggregates forming the inlet products. Indeed, we notice a slight evolution of specific surface (20 to 30 % increase), while the median diameter of particles is greatly reduced by the milling action (to less than 1 μm). This action tends to stabilize relatively quickly (less than 90 minutes depending on operating parameters). Extending milling time beyond this duration enables to improve micro-homogeneity through the constant repetition of agglomeration / fragmentation. Cohesivity of agglomerates also increase with milling duration.

On a technological plan, ball milling answers also perfectly well to the specifications that have been listed before. Its simplicity of design and working, the absence of fragile and complex moving parts confers it a great reliability and maintainability.

At the end of a milling batch, the separation between the grinding balls and the milled powder is easily done through a coarse grid. The powder is collected in the transport jar that has been remained docked to the tank during the entire milling operation. The vessel is kept under rotation during the emptying, so retention in the tank is very limited.

Finally, a ball mill is highly robust equipment. As described before, its working can be easily mastered with a few parameters and no particular tuning is needed from one batch to another. There is no risk of blocking or breaking of moving parts and heat power generation is less important than in highly energetic milling equipment, so there is no problem of heat evacuation or overheating of the powder.

Industrial feedback from existing plants

Ball milling has been successfully used for a long time in CEA (Cadache), COGEMA (MELOX and Cadache) and BELGONUCLEAIRE (Dessel) fuel manufacturing plants, on a large variety of powders (different types of uranium oxides, plutonium oxide, and scraps). By the end of 1997, more than 500 tHM LWR MOX fuel (70% of the world's cumulated MOX production) have been manufactured on an industrial scale in these plants by using the MIMAS process including a ball mill to perform the master mix. In the year 2000, the same process will have produced more than 1,000 tHM of LWR MOX fuel, by COGEMA and BELGONUCLEAIRE.

Operational feedback and a constant R&D work in collaboration with the CEA had enable to steadily optimize the performances of ball mills. In particular milling time have been appreciably reduced, leading to higher productivity and better outlet products characteristics (milling time is about 4 hours today).

Thanks to its high performances, ball milling enables today to recycle up to 70 % of scraps in the master blend (scraps are characterized by a low sintering reactivity making difficult its recycling).

Finally, due to the characteristics of the outlet product in a ball mill and to the specificity of MIMAS type processes (final dilution with UO_2), it is worth noticing that no sphereodization or granulation step is needed. The flowability of the final mixed powder is convenient to directly feed the press.

However, the best feedback from the operating plants concerns the quality of the end products. Electron probe microanalysis performed on sintered pellets show that local plutonium concentration in the ceramic is always inferior or equal to the Pu content of master blend, which guarantees a high solubility of the irradiated fuel.

This is confirmed by the two industrial campaigns performed at La Hague in 1992 and 1998, which have confirmed the feasibility of MOX fuel reprocessing.

CONCLUSION

COGEMA group has a unique experience in recycling industry and MOX fuel manufacturing. Feedback from operational plants, added to a constant R&D effort, enables to steadily improve the existing processes in order to propose to its clients the best technical and cost effective solutions.

In case of milling, this experience has led COGEMA to select in a first time ball milling as the best suited technology to fit its requirements, then to optimize the operating conditions of this equipment in order to improve its productivity while keeping its high level of performance.

Client specifications on sintered ceramic are widely respected, showing that ball milling provides the required micronization and micro-homogeneity of powders.

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Figure 1: U/Pu fuel manufacturing processes in France

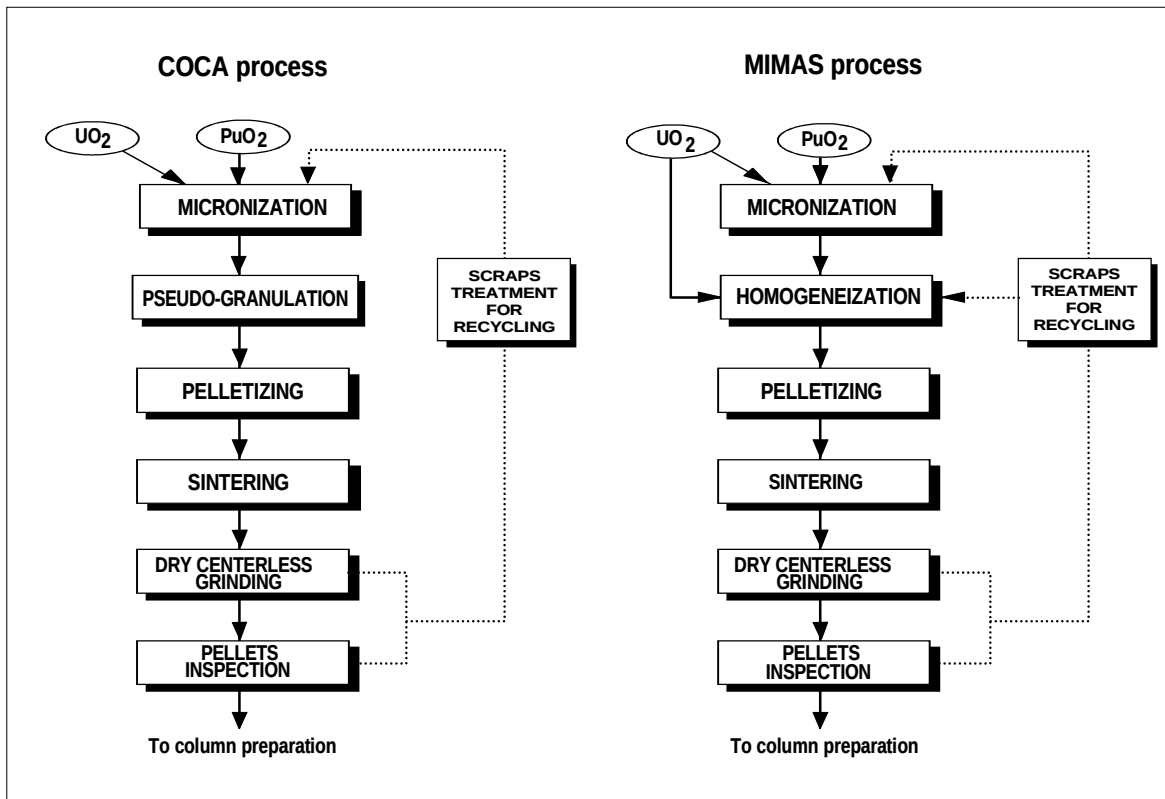


Figure 2: ceramification process for plutonium immobilization

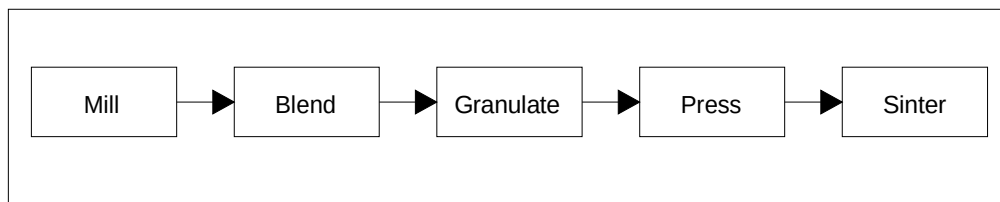
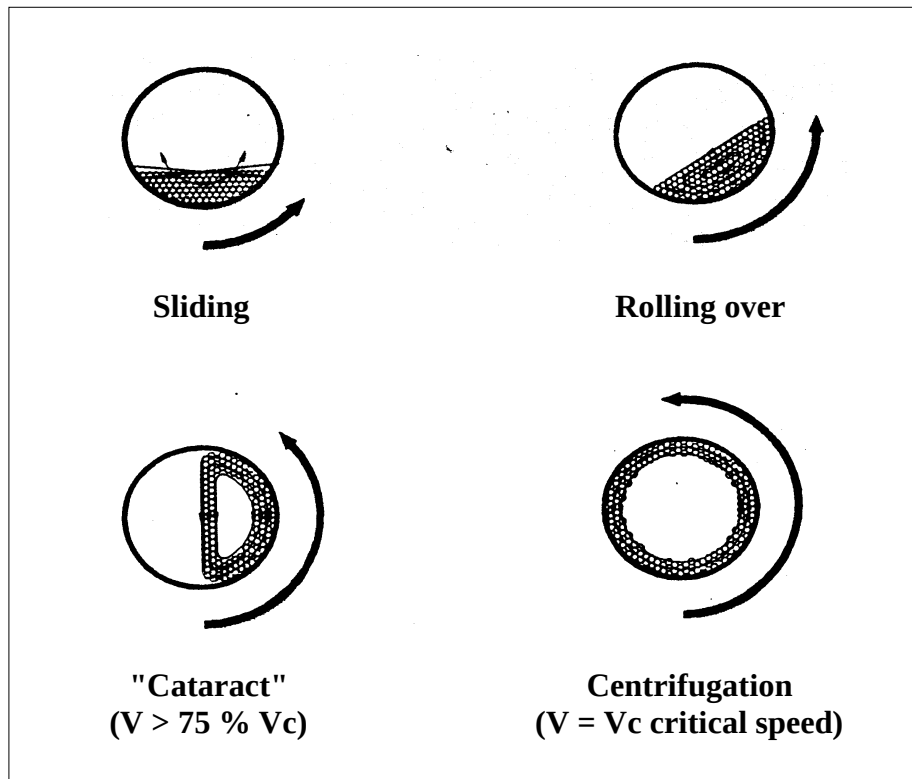


Figure 3: working of a ball mill, in function of the rotation speed

Figure 4: evolution of the specific surface (normalized by the initial value) and the median diameter (in volume) of an UO₂ powder in function of milling time