

## **Up-Scaling Methodology to provide knowledge for a process book: Application to a cementation process.**

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### **ABSTRACT:**

*This paper describes an up-scaling methodology applied to a cementation process. The final goal is to produce a formal document which describes the process and the associated technology by using the expected product characteristics. First of all, the size of the mock-up test platform and the volume of the end-product are taken into consideration. Either the demonstration can be carried out on a full-scale drum or modeling must be prepared to consolidate the specifications sought. Examples are given in the paper. The test methodology is described and includes six pilot trials. In the first phase the volume of the product is gradually increased and technology adjustment must be necessary. Therefore the nominal and the sensitivity tests enable the determination of the operating parameters, guaranteeing that the mortar produced has the same properties as that obtained in laboratory. The transient and degraded tests enable definition of the operating parameters and the procedure to maintain plant safety, to protect the process equipment and the material. Finally, the main objective of the extended long-term testing is to demonstrate that the operating parameters remain operational over a full production campaign.*

*This qualification program for the cementation of sludge from decontamination effluents enabled an approval request file for a new mortar package production using the cementation process to be prepared.*

## **I. INTRODUCTION**

Unlike high level radioactive waste which needs to be contained in glass, many low level or intermediate level radioactive wastes can be contained in mortar via a cementation process. Numerous cementation processes are available, with a choice among various technologies to produce the “primary mortar containment matrix” in a package (a drum, for example).

In France, a new cementation process and a new (unknown) mortar must receive approval from the agency responsible for the waste repository and from the nuclear regulatory authorities before any industrial production can begin. For the CEA, the approval process requires R&D trials at semi-experimental scale (also called semi-pilot scale) to be carried out with a technology close to that planned for the industrial platform in charge of the final waste treatment. The CEA Marcoule is working on the development of cement-based and geopolymers mortars at laboratory scale and at semi-industrial or even industrial scale as containment matrices for these wastes. The LTAP (Process cycle Advanced Technology Laboratory) is in charge of scaling up and developing the processes for conditioning these waste forms.

This paper concerns a process qualification methodology first developed and tested on glass fabrication [1], and adapted for the cementation process. The first cementation project consists in a mortar fabrication for conditioning the sludge from an effluent treatment station [2]. This methodology was successfully applied to containing heterogeneous solid metallic pieces in a fluid mortar [3] or to containing homogeneous small-sized solid particles. Thus this process qualification methodology has proved to be adaptable and can be applied to other subjects.

The article consists of two parts, with the first giving the organization of existing knowledge in documents (the process book, the piloting mode and the waste package technical specifications) which are described associated with the semi-pilot trials performed. This part also describes a series of conditions which enable the scale-one transfer operations to be prepared, for example by dimensioning the test volumes and the size of the apparatus necessary. The second part gives a description of the tests to be carried out on the platform, with illustrations of the equipment, the products, and the operating conditions for the cementation process.





Fig. 2: Waste reconstitution: filtration, and photo of sludge before cementation



Fig. 3: (Left) real scrap magnesium waste (Right) simulated magnesium waste

In the second example, the waste is a magnesium cladding which must be contained in a geopolymer matrix. The admissible void fraction for heterogeneous waste is only a few percent, which means that the cementation material must fill all the available cavities. Thus controlling the viscosity is crucial to ensure effective immobilization of the solid waste, and the shape of the simulant had to be very close to the real material.

### 2.3 Documents produced from semi-pilot scale trials

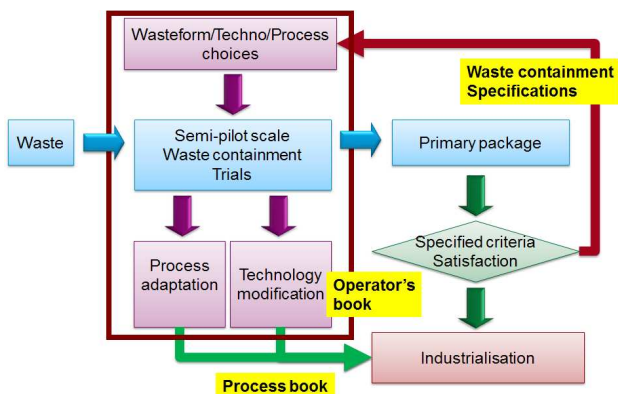


Fig. 4: documents produced from semi-pilot scale trials

This flow sheet gives the logic for the trials, with the yellow boxes showing the positions of the documents to

produce in order to industrialize the process, with the associated technologies. The test must first be defined, choosing the matrix package volume to be produced (in a large amount) with the operating conditions and the associated technology and equipment. These trials are repeated with improvements until a satisfactory primary package can be produced.

When a satisfactory result is obtained, it must be reproduced to guarantee that a robust process/technology couple has been found. The three R&D documents contributing to the industrialization and to the future operation of the industrial machine are:

- The process book, which is the main document interesting the design engineers who prepare the pre-project phases (in French, APS or “avant projet sommaire”). This book first describes the process perimeter, with its requirements for material input and output flows.
- The primary package specifications (of particular interest for the authorities) with the associated construction projects, for their future operation and operators. These specifications may be much wider than those initially imposed during the test (specified criteria) and, in the case of the production of our mortars during the cementation, may be:
  - A liquid mortar viscosity at fabrication within the range defined by the formulator
  - Absence of sweating (supernatant liquid on the mortar) 24 hours after the preparation
  - Matrix homogeneity throughout the package matrix volume
  - No excessively high temperature reached during hardening (specific limit for each material)
  - Limited shrinking of the materials produced (measured on molded samples during production)
  - Satisfactory mechanical resistance to compression checked after 1 month, then 3 months
- The equipment piloting mode, which interests future operators as well as the industrial machine manufacturer. It should be noted that the specifications for this industrial equipment include the technological modifications carried out or considered for the R&D semi-pilot machine, which may also be a prototype.

### 2.4 Full-scale drum modeling

Modeling may be a solution to replace the actual production a scale 1 package, in the situation where the size of the package required exceeds the capacity of the semi-pilot. Nevertheless a large-scale package must be made to maintain

a reasonable representativity and to understand any homogeneity problems at such a scale. In all cases, a reduction factor of scale 1/10 would be the minimum.

In the following example, the focus is on the temperature reached during mortar hardening in a 1.4 m square cube, whereas the largest package actually produced had 1 m sides. The volumes involved are respectively 2.8 m<sup>3</sup> and 1 m<sup>3</sup>, giving a factor of 3 between the digital and physical R&D objects. The modeling takes into account the geometrical shapes of 220 L or 380 L cylinders physically manufactured, and their associated instrument readings.

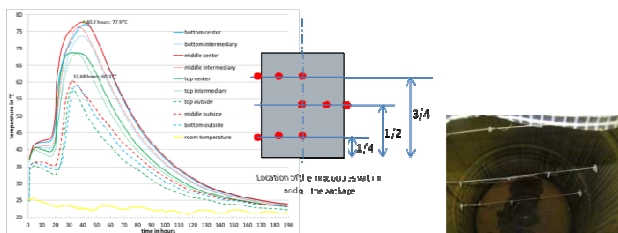


Fig. 5: Diagram of temperature evolution on and within a 380 L package (scale 1) during hardening

The thermal hardening time was between 20 and 60 hours. The semi adiabatic calorimetry and internal package measurements were similar. Such a duration gives enough time for the operator to move the package to the drying area. Should an accident occur on the mixer, the length of time before hardening means the issue can be dealt with, for example by emptying the mixer manually. The time is not so long as to negatively impact the monthly production rate.

With this type of measurement on several geometrical shapes, it is possible to model the power as a source term power linked to the reaction heat, and extrapolate by using a three dimensional modeling of the expected temperature results for a scale 1 package.

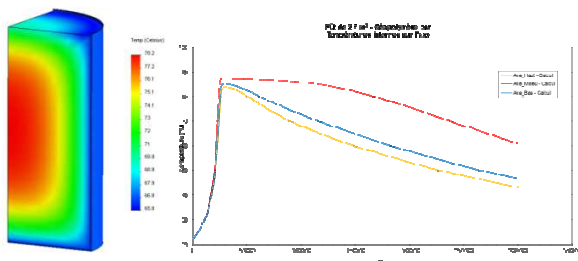


Fig. 6: modeling of the temperature in a scale 1 package (not manufactured)

## 2.5 Checking good agreement between the characteristics of materials produced in laboratory and those produced at semi-pilot scale

The mortar samples collected following the pouring were characterized in the R&D semi-pilot platform and compared to those of the formulation laboratory. These fresh mortar characterizations concerned their density, viscosity, hydrating heat, as measured by Langavant semi-adiabatic calorimetry, and hardening time, measured with a Vicat prisometer. The instrumentation of the packages with thermocouples enabled temperature changes to be recorded during mortar hardening. In each case and at each step of the trials, similar results must be found before going forward into the scaling up trial program.

## III. UP-SCALING PROCESS TRIALS METHODOLOGY

The process qualification program included six types of tests to specify the conditions necessary for a homogeneous material to be obtained.

- Up-scaling from laboratory to semi-pilot size: gradually increasing the size of the fabrication
- Tests to determine the nominal operating parameters guaranteeing the quality of the material fabricated at industrial pilot scale by final characterization of its physical and chemical properties compared with the same material synthesized in the laboratory.
- Two types of sensitivity tests:
  - A chemical composition sensitivity test similar to laboratory studies intended to synthesize the potentially most difficult mortar composition to fabricate at full scale, considering the technological performance possible from the selected cementation process.
  - Tests of sensitivity to the operating conditions, to specify possible parameter variation ranges acceptable for the material and for the process. For mortar fabrication, the parameters are the order of reagent introduction (waste, sand and cement), the stirring speed for each step of these additions and those of the final mixing. Besides these parameters of prime importance, others such as the power of the stirring equipment or the temperature are followed.
- Transient mode tests to determine campaign parameters: management of the rinsing effluent and the impact on the material of a long stirring time before pouring.
- Degraded mode tests to identify procedures for offsetting or mitigating the impact of incidents on



safety, on the process equipment, and on the material. The following degraded modes were investigated:

- the impact on the mixer if it is impossible to open the pouring valve,
- the impact on the mortar when stirring is halted for a long time.
- Extended long-term testing, with the main objective of demonstrating that process operation is not subject to variation, that the operating conditions specified for nominal operation as well as during transient phases are applicable, and that the material properties remain constant over time.

In this program, the tests chosen for these mortars were based on their rheological, homogeneity and mechanical properties, on the risk of water remaining on the mortar one day after pouring, and on the internal temperature reached during the hardening step (transformation of the liquid mortar into a solid compound). These tests were carried out on a full-scale pilot described below.

### 3.1 First step of the methodology: up-scaling from laboratory to semi-pilot size

To reach our objective of producing a scale 1 package based on a formula only prepared in the laboratory, the volume of the package was increased progressively by steps. Thus, in the following example, to work towards the production of a heterogeneous 220L package, 4 types of intermediary package were prepared. The first, of 32 liters, was not able to be produced until after a mortar composition modification by the formulator. Thus the first step enabled a consolidation of the matrix formulation. In the second type of trial, a simulant for the pieces to be heterogeneously contained was included. The interest of this was to test the mortar fluidity, to note any possible blockage defects in places which were difficult to access. Next, packages of 47 L, then 120 L, and finally 220 L were produced to monitor matrix homogeneity and to check that temperatures reached during hardening were under control.



Fig. 7: Examples of different increasing fabricated volumes



Fig.8: Examples of different technologies

Preparing these different ever-greater volumes often requires the use of different technologies and equipment. The figure above shows a planetary-movement mixing bowl used for mixtures of up to 5 L, a blade stirrer to produce up to 50 L, a stirrer with rotor/stator to strongly shear certain matrices, a concrete mixer to produce up to 220 L and a high-power mixer to prepare packages of up to 400 L in 2 batches, for example.

### 3.2 Second step of the methodology: nominal tests

The objective of the nominal tests was to define the nominal parameter values to synthesize a homogenous reference mortar with the same properties as the laboratory reference mortar. The operating parameters were defined by preceding tests without cementation, and could not be modified during the cementation process. Only the temperature in the mortar, the stirrer rotation speed and duration, the addition order of reagents and the flow rate were able to vary. The final choice of the nominal parameters depended on the results of the mortar characterization and the stability of the process operation.

The parameters monitored during the trials were variations in:

- the dosing and mixer masses,
- the rotation speeds of the tool and of the mixer vessel,
- the electrical power used by the tool.

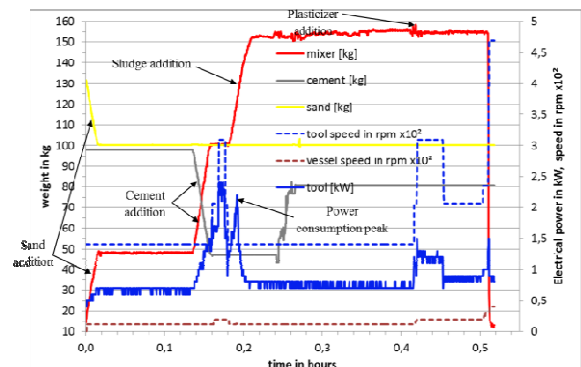


Fig. 9: Example of a batch production time flow graph

The power consumed increased greatly at the beginning of the sludge addition step, to reach a peak of between 2.5 and 4kW depending on the tool rotation speed (see Fig. 9). It then decreased just as quickly and leveled off. In the presence of liquid (for example, from the sludge), the solid particles, particularly those of the cement, tend to agglomerate at first. As the tool torque increases, the electricity consumption rises. Once the mixture is homogenized (i.e. when the stirring energy and the quantity of liquid enable dispersion of the solids), the mixture's viscosity decreases and the tool torque lowers, leading to lower electricity demand. This point can help check that the mixing is satisfactory. In the future production unit mixer, each batch will produce a 380 liter package. A package produced with the pilot platform mixer needed 4 or 5 successive batches to be made in order to reach similar operating conditions, i.e. a mixer fill rate of approximately 50%.

The ingredient additions and the phasing of the different mixing steps for the trial run is described in Table 1. The sludge was added after the dry materials in order to obtain a good mixing of the latter ingredients during steps 3, 4 and 5, as well as for future nuclear safety reasons. If the sludge was added first, any malfunction of the dry material dosing system, or even of the mixer during the stirring, would mean the sludge would have to be emptied into the container docked below the mixer so that repairs could be carried out. The processing of the resulting package non-conformity would be complicated to manage.

Step N°	Tasks	Mixing tool speed (in m/s)	Vessel speed ( in m/s)	Time in s
1	Sand addition	3.0	0.59	200
2	Cement addition	3.0	0.59	400
3	Mixing	4.3	0.94	30
4	Mixing	6.5	0.94	30
5	Mixing	4.3	0.94	10
6	Sludge addition	3.0	0.59	840
7	Superplasticizer addition	4.3	0.94	60
8	Mixing	6.5	0.94	120
9	Mixing	4	0.94	180
10	Preparation for emptying	5	1.38	10
11	Emptying	≈10	1.81	20
Total				1900 (≈31 min)

Table 1: Mortar package preparation protocol for the mixer

The ingredient addition times are long, and take a total of twenty-five minutes. This slowness is linked to the dimensioning of the future production unit:

- Limit the feed pipe section in order to minimize hold-back and rinsing water volumes,
- Avoid sudden pressure variations within the mixer during the additions.

In trials carried out on the test platform, the ingredient addition times were shorter and so in order to respect the protocol, longer mixing times were programmed in.

During the ingredient addition steps, the tool and vessel rotation speeds were set at the minimum to limit material heating.

The five minutes of mixing programmed for steps 8 and 9 ensured a homogeneous mixture in all the different cases studied during the trials.

The mixing parameters were optimized to ensure a good mortar mixing and to limit its heating during the thirty-one minutes of stirring. This aspect of the trials is not described further in this paper.

No water sweating could be seen on the package surface 24 hours after hardening, in conformity with the criteria imposed by ANDRA.

Core-drillings and visual inspections of cut sections were carried out (see Fig. 10)



Fig. 10: 380 liter package cross-section and samples

Macroscopically, the matrix was homogeneous for all the samples and showed no irregularities, for example sludge aggregates or liquid phases. The percentage of surface anomalies observed was 1%. Defects include pores between 2 and 5 mm in size, and a few desiccation cracks in the upper part of the package. The breaking patterns are essentially inter-granular, between the binding paste and the silica sand load.

The compression resistance tests for molded and core-drilled 11 x 22 cm samples tested after 90 days gave results between 17 and 30 MPa. These values are considerably higher than the 8 MPa required.

The thermal gradient in the package was 30°C between the outside and the core.

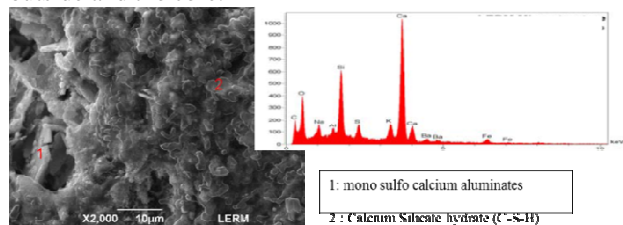


Fig. 11: Microstructure details

The microstructure is micro-porous, homogeneous and moderately cohesive. It is made up of calcium silicate hydrates (C-S-H). A few acicular ettringite crystals are also present in the micro-pores. The peaks for iron and for barium, elements which were significantly present in the waste, are similar on the different spectra. The absence of expansive mineral species and/or of harmful products, at the scale of the samples examined and at the end of the observation period (3 months), is encouraging for the long-term behavior of the matrix.

The characterization results for the mortars produced on the pilot platform at a semi-pilot scale were in conformity with those obtained in laboratory.

The analyses of the reference mortar produced under nominal operating conditions show that the mortar remained homogeneous. Very good agreement was observed between the theoretical and expected mortar compositions and the chemical analysis results. The following remarks concerning the deviations observed are applicable to all the tests.

### 3.3 Sensitivity tests

The first type of sensitivity test concerns the reliability of the matrix composition to be produced at an industrial scale. The objective is to be sure of the cement formulation robustness, validated for a medium-composition effluent. Following the complete study carried out at laboratory scale, a few critical compositions must be retained for scale 1 tests on the cementation pilot. As an example, in the case of STEL (liquid effluent treatment station) sludge cementation, 4 general compositions were tested: 2 sludge samples with high viscosity and salinity characteristics, and 2 others with low salinity representative of the STEL rinsing effluent. Four 380 L packages were produced to investigate these critical points, and issues related to homogeneity (segregation) were noted for the least saline

sludge. The solution found for this case was to recommend adapting the plasticizer content to later give more flexibility to the STEL operator's specifications.

The second type of sensitivity tests concerned the process operating conditions: the impact of the stirring conditions on the material quality. The test objective was to determine an operating range for these parameters. Generally, the minimum and maximum limits are identified for each of the operating conditions following expert advice. Several trials are then planned, coupling several extremes of these conditions (i.e. imagining the worst possible effects, either for the matrix or for the equipment). For example, a combination of a minimum mixing speed with a minimum mixing duration is critical for a homogeneous matrix to be obtained. Similarly, coupling a maximum mixing speed for a long duration with the highest-viscosity mortar is critical as concerns equipment physical capabilities, particularly for the stirrers. In each case, obtaining satisfactory packages without negative impact on the equipment enabled these limits to be qualified, defining the operating domain. This domain is then described in the process book.

### 3.4 Transient operating modes

During the transient operating phases, the operating parameters must be adjusted or additional operations must be undertaken to guarantee the homogeneity of the material or, at the end of the cementation campaign, to ensure the mixer wall surfaces and internals are as clean as possible, corresponding to their condition before the cementation operation. Thus the rinsing operation is very important, and must be included in the trial programs.

Vessel cleaning was carried out by a single rotating nozzle, but the trials showed that parts of the internals were not reached. For example, the tool structure created a "shadow zone" (see Fig.12). The industrial mixer will therefore need to be fitted with a second rotating nozzle as well as with fixed nozzles to clean these areas. The scraper limits the mortar hold-back on the bottom and walls of the vessel, just leaving a thickness of less than 2 mm. Carrying out intermediary rinsing and the design of a top with fewer holes and corners will simplify the final cleaning operation.

As a general rule, the right angles between parts (vessel, emptying pipe) were replaced by rounded shapes, thus limiting material hold-back.

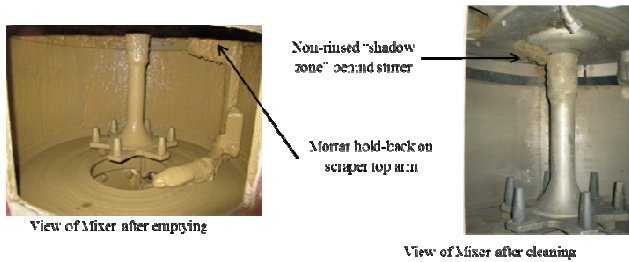


Fig.12: Platform mixer internals

The nominal tests, the sensitivity tests and the transient operating mode tests covered nominal process operation. The next requirement was to investigate degraded modes and to carry out an endurance test to finish the process qualification study.

### 3.5 Degraded operating modes

Operating incidents can cause the process to deviate from nominal operating conditions. Degraded operating modes must be examined to minimize their impact on safety, on the process equipment, and on the material. Means of detection are determined and management procedures are defined. In our case we chose to study one degraded mode: the impact on the mixer if it is impossible to open the pouring valve.

The mixer rotates constantly. The objective of the trials was to determine how the operator should pilot the apparatus in this degraded situation. The problem is so serious that a manual system, for example a manual hydraulic pump, could be a solution to open the pouring valve trapdoor. This operation, which would take a certain time, could exceed the nominal mixing period. A duration of 4 hours seemed globally sufficient in this test to carry out such an intervention. Thus the test was performed to find out what the consequences could be for the matrix and for the equipment. The trials showed that the increased mixing time led to a decreased material density, as the prolonged mixing added air to the mixture and meant a slight decrease in the mechanical properties. However the value remained largely above the specifications required.

The extended mixing time led to a temperature increase and therefore to a faster hardening time and greater viscosity. This in turn meant a considerable rise in material retention (hold-up) in the mixer after emptying, but which could be removed by normal rinsing.

Another degraded mode test consisted in emptying the mixer while the stirring parts were stopped. In this case the objective was to note the effects of a total loss of electrical power at the end of a mixing cycle and to determine the piloting necessary. In the first test, the emptying trapdoor was opened just after the machine stopped. The emptying

took place relatively satisfactorily, unlike the situation during the second test when the material was left to stagnate immobile in the mixer for 4 hours. The emptying operation was then impossible, and only after stirring started again, fluidifying the matrix, could the mixer be emptied. The R&D trials therefore enabled a warning to be given to the project team, who could for example plan to connect the rotation motors to a backup electricity network.

As the packages produced were in conformity with the specifications, the two piloting recommendations were added to the process book and to the piloting mode.

### 3.6 Endurance test

The main objective of the endurance test was to demonstrate that the process is not subject to variation, that the operating conditions specified for nominal operation as well as during transient phases are applicable, and that the material properties remain constant over time.

A time of 20 to 30 minutes is necessary between two batches for the package transfer and vessel rinsing operations, and to prepare the unit for the following package production.

Following these trials, a production scenario for the future cementation unit was prepared. The future workshop will operate non-stop. Each campaign will enable the production of 9 nominal packages and 1 special package of rinsing effluents.

In the case of this study for the cementation of viscous sludge in a mixer, 2 elements subject to variations needed to be investigated. Firstly, the hold-up in the machine after each batch could not vary significantly, and needed to remain constant throughout the campaign. This means that the internal surfaces do not change and that the mortar does not solidify on the mixer walls. The second element is the need to be sure that at the end of a campaign and after a conventional rinsing, the state of the mixer internal surface will be identical to its condition before the campaign began.

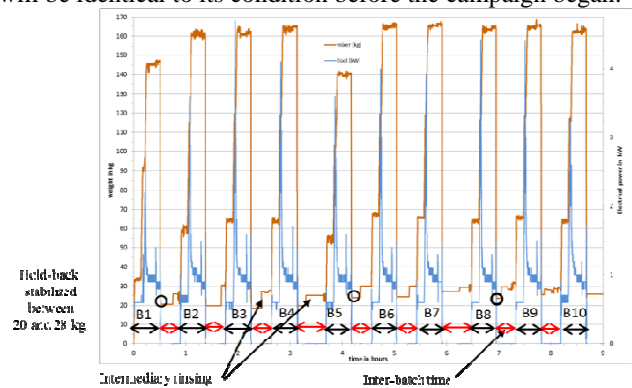


Fig. 13: Production campaign running diagram



In the figure above, ten successive batches can be followed with the orange curve, which represents the evolution of the mass in the mixer, and the blue curve which gives the changes to the electricity used to carry out this mixing. After each emptying, it is important to monitor the mass remaining in the apparatus and it can be seen here that the hold-up which was 20 kg early in the campaign increased somewhat to reach about 26 kg at the end. This result partially validated the endurance test.

#### IV. CONCLUSION

This methodology gradually enabled the process to be qualified. By beginning with the tests under nominal operating conditions, i.e. the nominal tests, the sensitivity tests and the study of the transient modes, it was possible to quickly detect possible issues, and thus to modify the operating conditions or the mortar composition range if and when necessary.

The study of degraded operating conditions identified ways of detecting incidents leading to such conditions and of implementing procedures to protect safety aspects, the process equipment and the material. In this application the degraded modes tested therefore had no negative effect on any of the above.

Finally, the endurance test validated the nominal operating conditions over an extended time period.

This process qualification methodology applied to the cementation of sludge from a liquid effluent treatment station enabled the package qualification file for new a containment mortar to be drafted. In addition to the technological data, this file also describes the study of the mortar composition range and the process parameters, which were carried out at the same time.

The trials enabled a production unit operation to be suggested, and a process book to be prepared. Modifications to the mixer design have been taken into account for the scale 1 machine. Future actions will now concentrate on the first startup trials for the unit, scheduled for 2016.

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