Production of a diluted solid tracer by dry co-grinding in a tumbling ball mill

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ABSTRACT

This paper presents a study on the production by co-grinding of a diluted solid tracer, sized less than 10 µm and containing less than 2 wt. % of active product, used in the field of grounds contamination and decontamination. Co-grinding was performed in a tumbling ball mill and permits to produce easily a diluted tracer without implementing several apparatus.
The two products were ground separately first and then together. The follow-up of the particles size and morphology, as well as the modelling of the grinding kinetics have permitted to propose a mechanism by which the diluted solid tracer is produced.
The influence of the operating conditions (nature and initial size of the diluting medium, ball and powder filling rates, proportion of the polluting tracer) on products grinding was studied. Thus, we have defined optimum co-grinding conditions permitting to produce a tracer offering the required properties. These ones are classical for tumbling ball mills.
This kind of mill is very interesting since its sizes can easily be extrapolated to answer to an industrial demand.

KEYWORDS: co-grinding, tracer, size, dispersion

1. INTRODUCTION

Different events may lead to accidental pollutions of grounds, present as traces. Ground cleaning up demands efficient means which are often to be developed. The development of cleaning methods first needs to produce an artificial pollution based on the dispersion of a contaminating agent, present at a very low proportion, in an inert medium having properties close to those of the ground.

The properties of such a particulate system are the following:

- the proportion of the pollutant has to be lower than 2 %;
- while the pollutant and the inert medium have different sizes and densities, the pollutant has to be well dispersed in the inert medium to confer an homogeneous pollution of the ground;
- all the particles of the two products need to have final sizes lower than 10 µm.

A usual preparation method to produce a diluted solid tracer consists of several steps such as impregnation, filtration, drying, reaction and grinding, which are realised in different apparatus. Co-grinding allows making such a product in a single apparatus that costs cheaper. In a previous study [1], we have shown that it was possible to disperse less than 5 % carbon nanotubes in a polymeric matrix. In another work [2], we have observed that silica could be ground to reach mean sizes around 3 µm.

In this study, it is proposed to produce, by co-grinding, a diluted solid tracer using an active agent dispersed in silica, the properties of which are close to those of grounds. Porous alumina was also tested. This operation was realised in a tumbling ball mill. Indeed, this process permits a reduction of the particles size. The shearing stress imposed in the grinding chamber favours a good dispersion of a product in the other one, even if the initial properties of the two constituents (size, density) are different. The production mechanism was studied, as well as the influence of the operating conditions on the characteristics of the final product.

2. METHODS AND MATERIALS

Dry batch grinding and co-grinding experiments were realised using a tumbling ball mill (figure 1). It consists of a stainless steel cylindrical chamber, 0.8 L in capacity, rotating around its horizontal axis. The chamber contains stainless steel balls with a size between 7 and 20 mm. The rotating speed of the chamber was fixed at 100 rpm, i.e. at 75 % of the critical speed. The ball loading volume and the powder loading volume are variable parameters for each experiment.

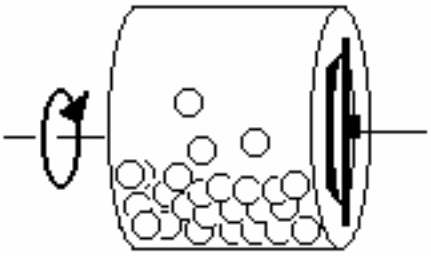

Figure 1: Tumbling ball mill

The vol. % of balls was fixed between 20 and 75 %, while the powder filling rate was varied from 20 to 50 vol. % of the void space between the balls.

The inert materials tested in the study were silica (sand of Fontainebleau with different sizes) and porous alumina. As for the active product, for confidential reasons, its nature will not be given here. Its proportion in the mixtures was varied from 0.5 to 2 wt. %. Some characteristics of the materials are gathered in table 1 and SEM photos of the products before grinding are presented in figure 2.

Material	Density (kg/m^3)	Initial mean particle size (µm)	Initial morphology
Silica 50-65 µm	2 080	60	Rectangular and angular
Silica 100-200 µm		160	
Unsieved silica		220	
Alumina	3 970	170	oval, ellipsoidal, porous
Tracer	6 500	56	Aggregates

Table 1: Characteristics of the materials

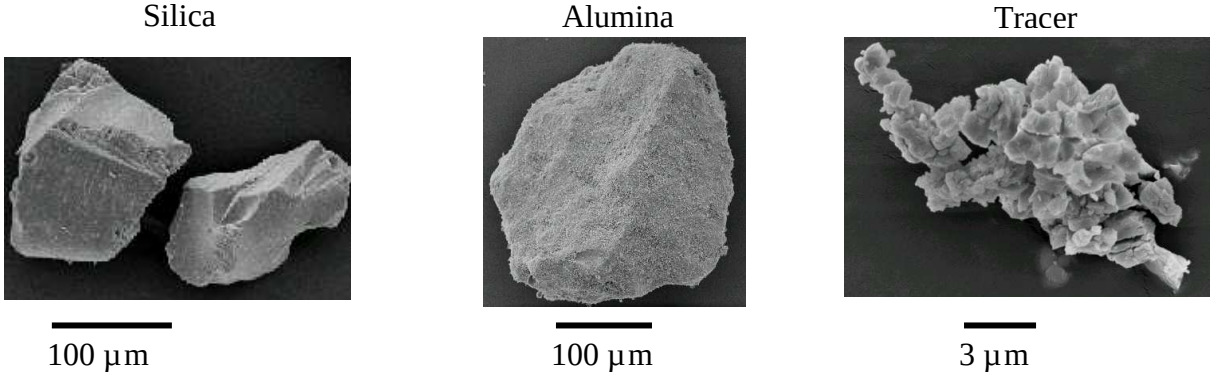

Figure 2: SEM photos of the products before grinding

The mill was filled with the balls and the powder to be ground, and then started. It was stopped at different times to take samples from various zones of the chamber. Since sample volumes were very small, it can be considered that the powder filling was not modified significantly during grinding.

Dry measurements of particle size distributions were realised with a laser diffraction granulometer (Malvern Mastersizer 2000). Particles were dispersed using a Sirocco instrument with adapted pressure for each sample measurement. The data were processed according to the principle of the simple diffusion and laser light diffraction. The calculations use the particle refractive index, enabling artefacts at small sizes of the distribution to be limited. This index is equal to 1.554 for silica and 1.780 for alumina. The mean diameters, d50, corresponding to the cumulated volume fractions of 50 %, were calculated from size distributions. The percentage of particles with a size higher than 10 µm (%>10) was also determined. These particles will be considered as “big particles” in the study. Different selected samples were analysed by scanning electron microscopy to observe the particles morphology. The particles were deposited on a double-sided carbon tape (diameter 12 mm) and were gold plated for two minutes. A dispersion system allows the particles to be well distributed on the tape and avoid their superimposition. Then the samples were observed.

The size distributions were modelled using Origin Peak Fitting package, which allows them to be expressed as a function of several statistical laws [3]. The log-normal law was convenient to describe the matrix fragmentation as well as the tracer grinding. This type of law can be written as:

$$f(x) = \frac{dW}{d\ln x} = \frac{1}{\ln \sigma_g \sqrt{2\pi}} \exp\left[-\frac{\left(\ln x - \ln x_g\right)^2}{2 \ln {\sigma_g}^2} \right]$$

where $f(x)$ is the volume fraction, W, is the cumulated fraction of particles sized less than x, x_g, the mode of the sub-population considered and σ_g, the standard deviation.

This software allows determining the various populations of particles present in the mill and their evolution during grinding.

3. RESULTS AND DISCUSSION

3.1. Size evolution of separately ground products

Firstly, the products were ground separately. Figure 3 shows the evolution of the size distributions of the silica initially sized 100-200 µm (35 vol. % balls, 30 vol. % powder), while the variations with time of the mean size and of the percentage of "big particles" (size > 10 µm) are shown on figure 4 for all the inert materials used in this study.

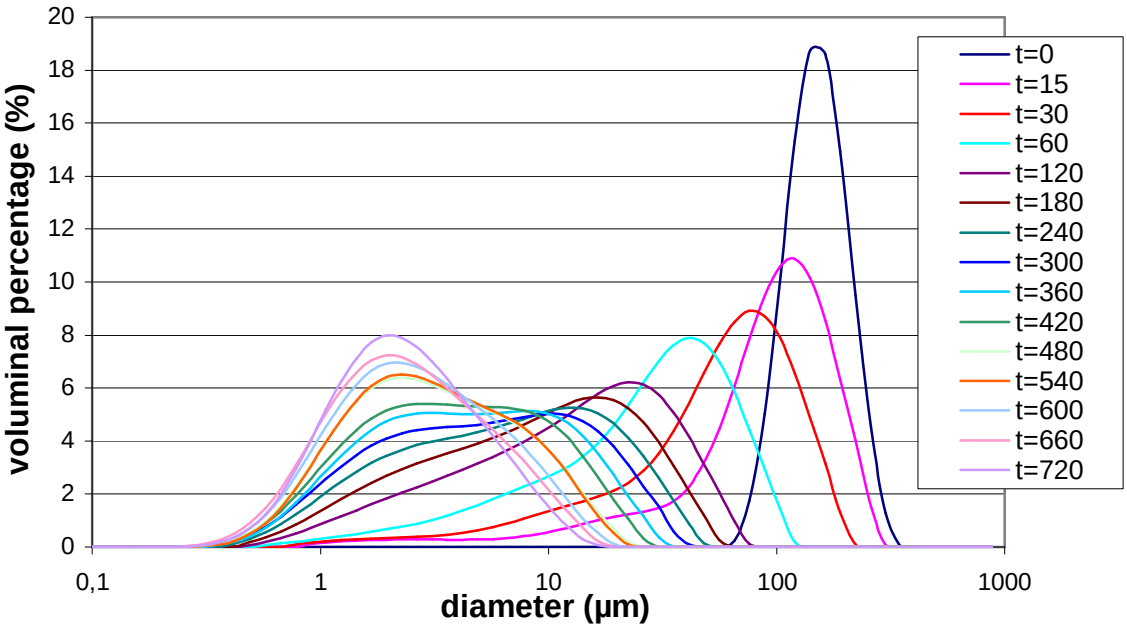

Figure 3: Evolution of the size distributions of silica during grinding (initial size 100-200 µm, 35 % balls, 30 % powder)

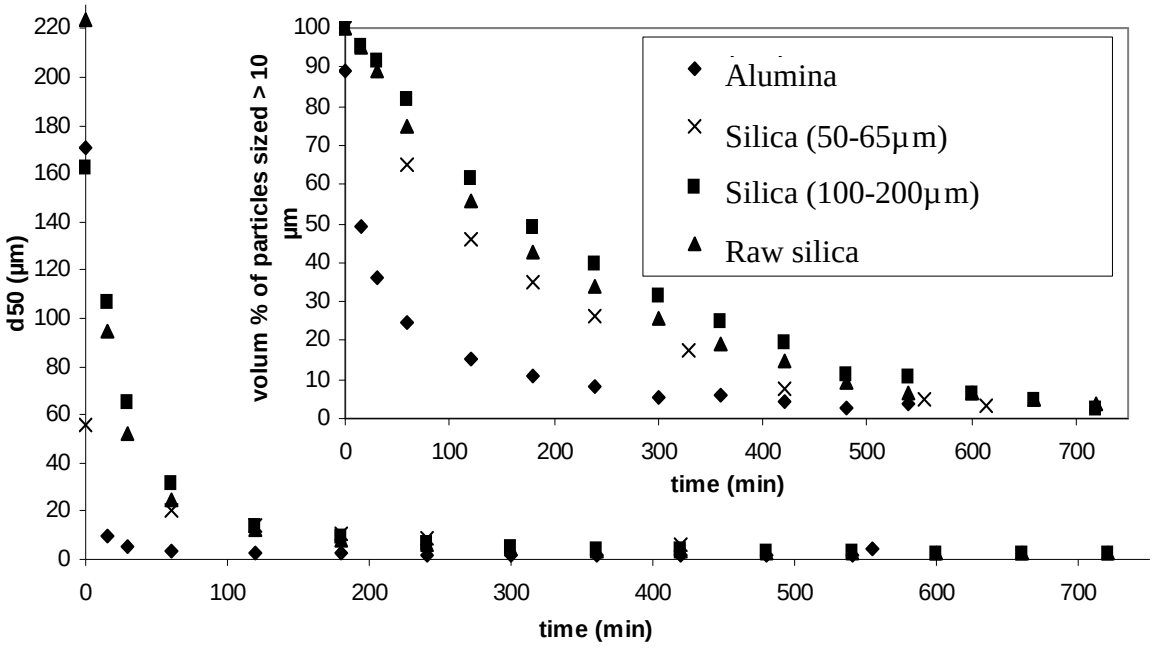

Figure 4: Variations during grinding of the mean size and of the percentage of "big particles" for all the inert solids (35 % balls, 30 % powder)

Initially, the size distribution is unimodal: only one tightened peak is observed. Then, this peak shifts towards the left, i.e. to the finer sizes. However, it becomes spread since fine particles are produced while particles with a size higher than 100 µm are still present in the mill. Progressively, these large particles tend to disappear to the profit of small particles. Finally, at the end of the experiment, the sample is mostly constituted of particles with a size lower than 10 µm. The changes are significant during the first 120 minutes, while they are less important then. At the end of the experiment, agglomeration phenomena are observed, since the right side of the curve at 720 minutes shifts towards big sizes. Figure 5 shows small fragments resulting from fragmentation, as well as a big particle on which fines are agglomerated. The same kind of evolutions has been observed with the alumina and the tracer, but the phenomena are faster with these two products than with silica.

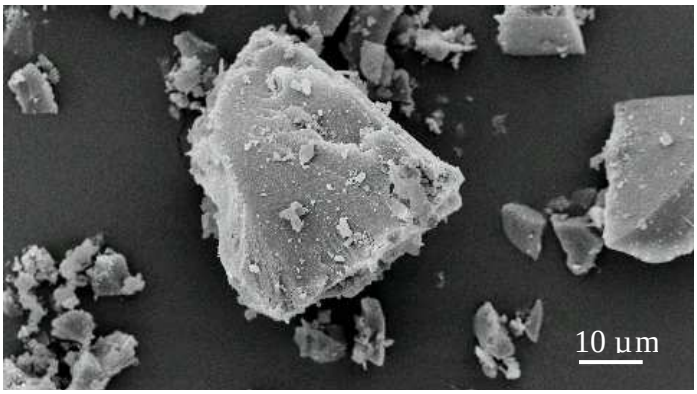

Figure 5: SEM photo of different silica particles

This leads to a rapid variation of the mean size during the two first hours. Then, the reduction is lower and a limit mean size of 3 µm is reached. Since a micronic size is needed, the second step of the size decrease is necessary, even if it takes a long time. Indeed, one of the constrains is to propose a particulate system containing the least possible of particles with a size higher than 10 µm. Figure 4 shows that the percentage these “big particles” decreases monotonously during 400 minutes. Then, the decrease is less important and the percentage reaches 3 % after 12 hours. Because the percentages are expressed in volumes, the number of particles having a size higher than 10 µm is low enough to be neglected.

As for the other inert solids (silica with other sizes and alumina), we have observed that the fragmentation rates are different. Indeed, concerning silica, the higher the mean size before grinding, the faster its reduction during fragmentation. Moreover, fragmentation occurs more rapidly with alumina than with silica. Indeed the chosen alumina is porous, what facilitates cracks propagations in the particles compared to massive particles. Consequently, the percentage of “big particles” decreases more or less rapidly, depending on the product nature and on the initial mean size and the time to reach 3 % of “big particles” depends on the inert medium. Nevertheless, even if the initial mean sizes and the fragmentation rates are different, the curves tend towards the same limit size of 3 µm which is generally observed for this kind of products during dry grinding [4]. Moreover, concerning silica, results are not significantly different with the three initial sizes. Since the two samples at 50-60 µm and 100-200 µm are obtained from the raw silica after sieving, this means that there is no use adding a sieving stage in the process. Thus, the following experiments were realised with the unsieved silica.

In other experiments, the balls and the powder filling rates were varied. Four values of the balls rate were tested (20, 35, 50 and 75 vol. %). The two extreme rates did not give satisfactory results. Indeed, a high rate induces a reduction of balls movement in the chamber, while a low balls rate reduces contact probability between the grinding media and the powder. Grinding efficiency is then reduced. The two intermediate rates offer a compromise between the two phenomena and fragmentation is enhanced. Results obtained with these two rates are similar. To minimize the powder consumption during the study, a ball filling of 35 % was retained. As for the powder rate, it was fixed at 20, 30, 40 and 50 vol. % of the void space between the balls. As it could be expected, the lower the powder rate, the faster the fragmentation and the shorter the time to reduce the proportion of big particles. However, due to a productivity constraint, the lower rate cannot be chosen. That is why the following experiments were realised using 30 % powder.

Finally, the tracer size reaches the limit value of 3 µm after 20 minutes. This indicates that its fragmentation rate is fast.

For a better understanding of the fragmentation mechanism, a study of the kinetics was realised. All the samples, even those of the single products, contain several particle populations. The objective is to identify the different populations and to characterize the variation of their proportions during grinding. Figure 6 presents the kinetic parameters for the raw silica. Initially, seven populations with big modes are present in the sample. As grinding occurs the modes are constant, but the populations fractions vary. These big populations tend to disappear because their fragments feed the intermediate populations and generate populations with small sizes. Then, the proportions of the intermediate populations decrease when these ones are no more fed by fragments from big populations. Intermediate particles are broken, and the fractions of the small populations increase. Finally, a new population (P5) is created at the end of the experiment and is certainly constituted of agglomerates of fine particles, because its proportion always increases with time while no bigger particles exist. The feeding of this population can thus only be due to agglomeration phenomena between smaller particles which disappear. Similar kinetic results were obtained with alumina but they took place more rapidly.

As for the tracer, initially one main population, with a mode at 88 µm, constitutes the powder, since it represents about 45 % of the sample. The percentages of the other populations are lower than 10 %. Big populations disappear during the first 30 minutes and the fractions of the small populations increase. After this time, the proportions of the different populations do not evolve significantly. Most of the populations present after 30 minutes in the mill chamber have modes lower than 3 µm. One can conclude that tracer agglomerates, initially present in the powder and shown in figure 2, dissociate rapidly to form individual crystals. Since the size of these crystals is lower than the limit size proposed by this kind of mill (several micrometers), their fragmentation is not possible and the fractions of the populations remains constant. Table 2 gathers the values of the modes determined for the raw silica, the alumina and the tracer.

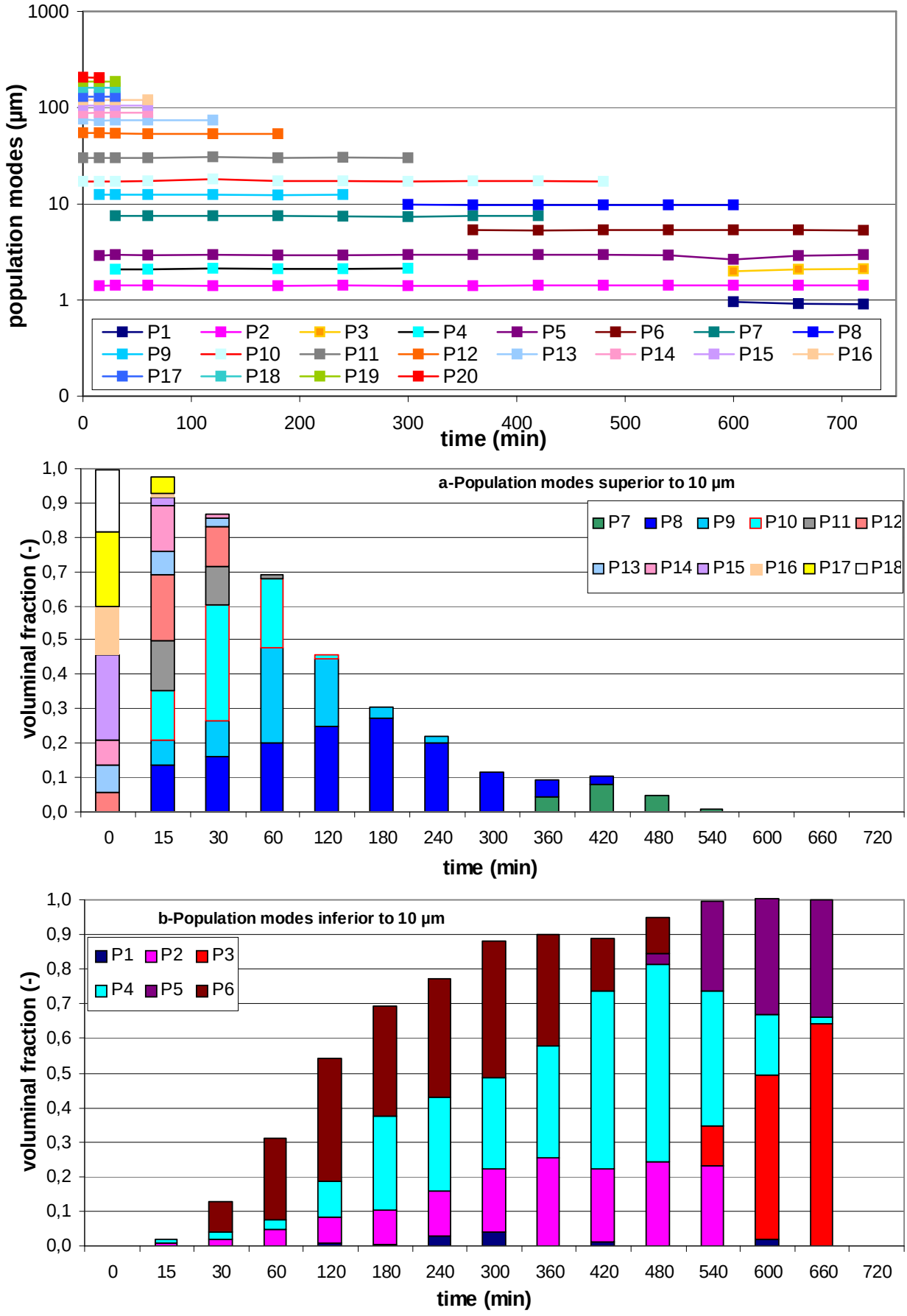

Figure 6: Kinetic parameters for the raw silica (35 % balls, 30 % powder)

Modes of populations determined with raw silica	1.4	2.8	17	30	54	75	105	130	160	185	206	244	331
Modes of populations determined with alumina	1	2.1	7.3	43.3	81.7	101	122	188	300				
Modes of populations determined with the tracer	0.6	1	1.7	2.5	4	6	14	20	30	43	60	88	130

Table 2: Modes of the populations determined for the raw silica, the alumina and the tracer

3.2. Size evolution of the mixtures during co-grinding

Figure 7 presents the evolution of the size distribution of a mixture containing 99 wt. % of silica and 1 wt. % of tracer (35 % balls, 30 % powder). The results on the variations of the mean size and of the percentage of "big particles" are shown in figure 8 for mixtures containing raw silica or alumina as inert materials. Since the tracer proportion is low, it does not influence significantly the evolution of the curves: the mixtures curves evolve similarly to those obtained with the inert materials alone. The tracer sticks rapidly on the surface of the inert material (figure 9) which breaks then as if it was a single product. Progressively, the stuck tracer aggregates are subject to attrition under the effect of the ball, and the removed fragments stick on free silica surfaces. This permits a significant reduction and a better dispersion of tracer particles. This was already observed in previous work with calcium carbonate as the filler, for which the particles size could be decreased until few hundreds of nanometres [3]. The same observations were done with mixtures containing other tracer proportions, and it was observed that the tracer fraction has no significant effect on the fragmentation rate in the ranges (0.5 – 2 %) fixed in this study.

A kinetic study was also realised with the mixtures. Initially one observe all the populations of the inert solids than those indicated previously (table 2), but also one population at 88 µm. This last corresponds to the main population of the tracer, and the other populations detected with this product when ground alone were not identified by the software in the mixture. This may be explained by the fact that their proportions in the tracer are low and the tracer proportion in the mixtures is very low. The unique tracer population disappears after 15 minutes, due to a breakage of the initial agglomerates and the agglomeration of the individual crystals on the inert particles. Then the behaviours of the various populations are identical to those observed during grinding of the inert materials only.

The co-grinding process permits to produce easily a diluted tracer without implementing several apparatus. The operating conditions are classical for tumbling ball mills and allow a good dispersion of the active agent in the diluting media. Furthermore, the sizes of such a mill can easily be extrapolated for answer to an industrial production.

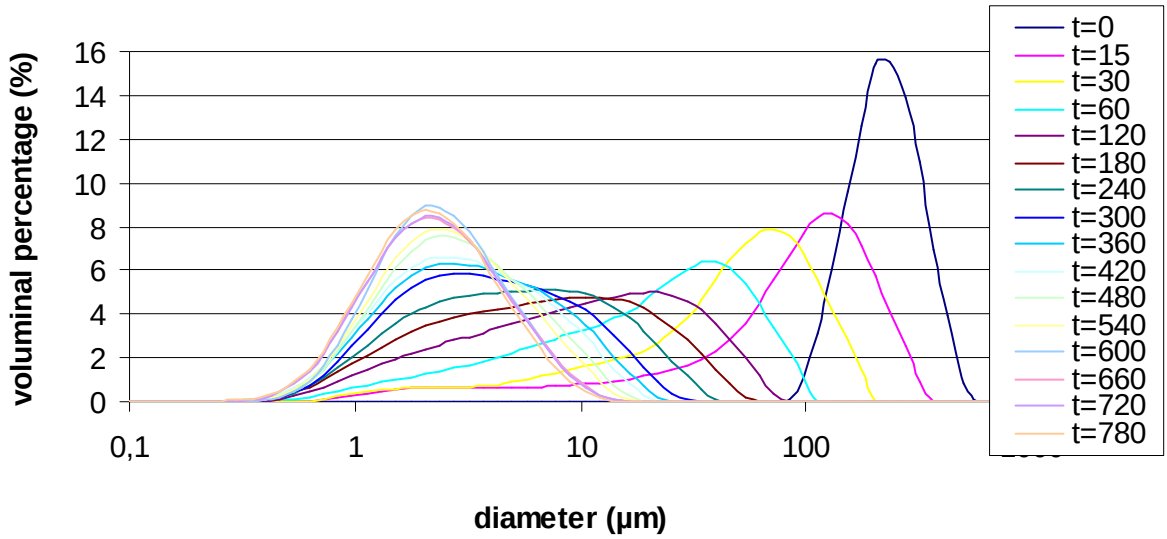

Figure 7: Evolution of the size distributions of the mixture raw silica - tracer during grinding (35 % balls, 30 % powder, 1 wt. % tracer)

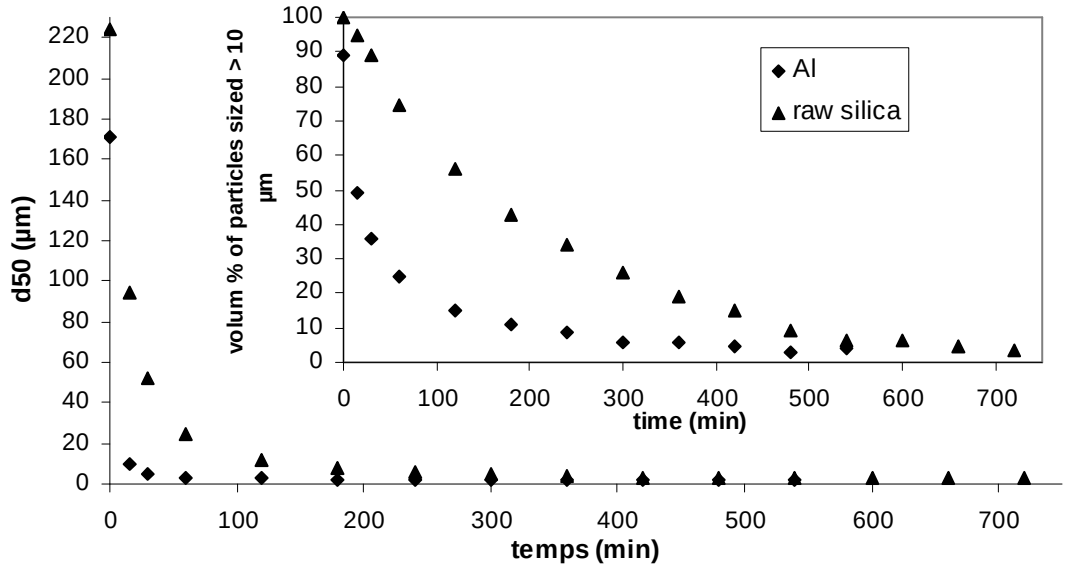

Figure 8: Variations during grinding of the mean size and of the percentage of “big particles” for the mixtures containing 1 wt. % tracer (35 % balls, 30 % powder)

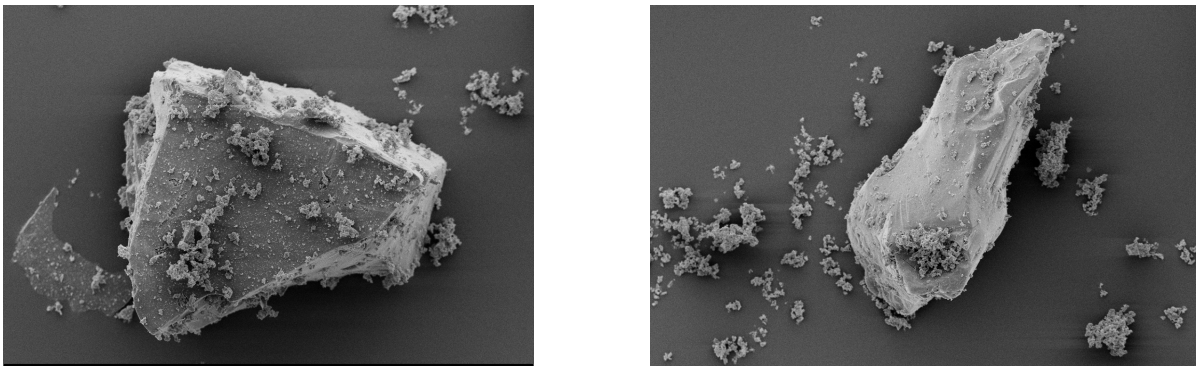

Fig 9: SEM photos of mixtures

4. CONCLUSIONS

The purpose of this study was to propose a new process permitting to produce a tracer diluted in an inert solid having properties close to those of soils. The tracer, present at a low proportion in the mixture, had to be homogeneously dispersed in the inert material, the size of which should be lower than 10 µm. Two inert products were chosen (silica and porous alumina), and co-grinding was used for this operation.

The three materials were first ground alone to analyse their behaviour during grinding, and the influence of the operating conditions on the fragmentation rate was characterized. The choice of the ball and the powder filling rate leans on a compromise between effectiveness and productivity. As for the effect on the inert material nature, the fragmentation rate is faster with alumina which is porous than with silica which is compact.

Mixtures of the inert materials and the tracer in various proportions were then co-ground, and similar curves were observed since the low tracer proportions do not influence significantly the behaviours of inert materials. The tracer agglomerates rapidly on the inert particles which behave as if they were alone in the mill. The co-grinding process permits a good dispersion of tracer fragments with a size lower than what could be expected with an individual grinding of this material. Furthermore, agglomeration phenomena permit to avoid a segregation of particles having different physical properties.

The mechanism by which the diluted tracer is produced was explained through a kinetic study.

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