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Solid fertilizers - Study on homogeneity

Engrais solides - Etude de l'homogénéité

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Solid fertilizers - Study on homogeneity

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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1   General

> NOTE — In the Council Directive 76/116/EEC [1] fertilizers are "products obtained chemically or by blending procedure". Further Directives of The Commission (77/535/EEC [2] and amendments/modifications) relating to methods of sampling and analysis for fertilizers do not distinguish between both types. Regarding this gap in the existing regulations, EC/DG III Fertilizer Group, EFMA addressed the question "how to distinguish between both types of EC fertilizer by labelling and the control of this labelling, pursuant to articles 8(1) and 8(2) of the Council Directive 76/116/EEC?"
>
> In anticipation of a "mandate to be initiated by the EC-Commission and in response to resolution CEN/TC 260 41/1993, WG 2 has agreed "to extend its work on this subject and will start with a literature search"(resolution 32 of WG 2) (see [3] to [14]).
>
> The results of this study are presented in this CEN Report.

Blending fertilizer materials together is an old technology to get compound mixtures. It is a special form of dry mixing in which the materials to be mixed are all granular or all powder fertilizers.

The mixing of solid materials is not a spontaneous process, mixing always involves relative motion between particles, it will be carried out in blending equipment in a more or less energy consuming operation. The degree of mixing may be influenced by the equipment used, the time of mixing etc.

The opposite of mixing is segregation. After having been mixed, the segregation of the mixed materials can occur.

Segregation occurs when individual particles in a fertilizer differ in physical properties (e.g. particle size, density, sphericity) to such an extent, that they respond differently to the mechanical disturbances caused by a handling process: disturbances caused by vibration during transportation, flow of the material over itself ("coning") or by ballistic movement. During these disturbances, particles of similar physical properties tend to congregate; therefore, the degree of mixing of the mix of particles is affected. However, segregation does not affect the fertilizer type to which the product belongs (blended or not).

If all the particles in a fertilizer were physically identical, no amount of handling would affect degree of mixing. If all the particles in a fertilizer were of identical chemical composition but of differing sizes, handling would include physical segregation but would not affect chemical uniformity.

> NOTE — In some cases visual inspection may identify blended materials, but there are fertilizers on the market for which the type can be decided only by an analytical investigation of the distribution of some property (e.g. nutrient content) within the product. Methods to measure the distribution of a property within a bulk belong to the category "homogeneity test" in a broad sense.

a) Homogeneity tests
Regarding test methods for degree of mixing the standardisation of fertilizer is a special case. Homogeneity tests could be used for different purposes:

    1) Identifying bulk blends as such
    2) Control of degree of mixing
    3) Comparison of mixers
    4) Optimisation of mixing time
    5) Check of blending equipment

This CEN Report will not only consider the practice of blending fertilizer but also take a broader look at the "state of art" of degree of mixing in general. See also [15] to [33].

First of all, in this CEN Report the sampling methods of fertilizer will be considered.

b) Test of the degree of mixing
In mixing tests, the statistical variation of the composition is used as a measure for the degree of mixing, expressed in some kind of index.

c) Indirect methods
Aside from mixing tests, in the practice of fertilizer blending, indirect methods are used for assessing the physical compatibility of the granular components. Such indirect methods are: Size Guide Number (SGN),

Uniformity Index (UI) Granulometric Spread Index (GSI), Mixing Quality Index (MQI). They will be considered in this CEN Report.

The general fertilizing aspects of blends and the chemical compatibility of the components are out of the scope of this CEN Report.

2 Sampling and test of the degree of mixing

2.1   If there is only one representative sample for a complete lot, there is no way to determine the degree of homogeneity of the lot due to the mixing of the individual increments prior to reduction and preparation of the laboratory sample.

2.2   The Commission Directive 77/535 EEC [2] in its Annex 1 ("Methods of sampling for the control of fertilizers") does not distinguish between chemically obtained and blended fertilizer. However in EN 1482 it is noted, that blended product can introduce additional sources of variation.

2.3   The sampling methods ISO 8633 and ISO 8634 refer to "increments of more than the minimum mass defined in ISO/TR 7553". The latter defines the requirement for sampling of "fertilizers composed of particles of the same nature" as well as for "fertilizer composed of particles of different nature". (ISO/TR 5307 does not distinguish between the two types.) However the ISO methods are focussed on the aim to collect representative samples for the whole delivery and not for homogeneity analysis.

2.4   ISO 7742 for reduction of samples and ISO 8358 for preparation of samples for chemical and physical analysis point out that the representativity of the sample may be lost during further subdivision and reference should be made to ISO/TR 7553.

All sampling methods emphasize that sample(s) taken should be representative for the whole delivery. Regarding homogeneity of the whole, the homogeneity of the sample(s) is the property that should represent the whole. For this case, no sampling method is known, so a test method for homogeneity should include sampling (especially number and mass of increments, special handling to avoid segregation, reduction of samples and so on).

2.5   Simple blend may be identified as such even in a well mixed representative sample before the grains are destroyed in a grinding procedure. For such blends a visual inspection of the grains (shape, form and color) is helpfull to pic up grains by similarity. For more sophisticated blends, when no or little apparent difference is given, only the chemical analysis of individual grains can decide "are they similar or not". The grains for analytical investigation may be picked up randomly before grinding of the sample as a whole.

3 The degree of mixing

3.1   The variance of the composition characterizes the mixture as a whole and this theoretically requires a knowledge of the nutrient content everywhere in the mixture. The variation (σ^2) of the nutrient content in a mixture is determined by two terms: the precision of the analytical method (σ^2_p) and the variance of the mixing (σ^2_m). The last term includes also sampling variance.

$$\sigma^2 = \sigma^2_p + \sigma^2_m \left(1 - \frac{g}{G}\right)$$

(1)

The factor g/G is the ratio of the particle size and the sample size (mass). If $g = G$, an individual particle is analysed, the variance of the analysis is only determined by the precision of the method. In special cases, for example the beginning of the mixing process, the total variation σ^2 is dominated by the mixing-term:

$$\sigma^2_p << \sigma^2_m \geq \sigma^2 = \sigma^2_m$$

(2)

In ideal mixing $(\sigma^2_m \geq 0)$ the variation is dominated by the precision term:

$$\sigma^2{}_m \ll \sigma^2{}_p \geq \sigma^2 = \sigma^2{}_p \qquad\qquad (3)$$

Practically, the empirical variances are based on a finite number of samples, so the variation σ^2 is unknown and must be replaced by the estimation s^2.

If the analytical values are normally distributed, the ratio s^2/σ^2 has a chi-square distribution, so the standard deviation for a finite number of samples is not a sharply defined value; being itself a statistical measure within certain confidence intervals. Corresponding to a certain probability level (normally 95 % or 99 %) and a known number of samples the true value of σ^2 will be found between the limits:

$$s^2 / \chi^2{}_u \leq \sigma^2 \leq s^2 / \chi^2{}_l \qquad\qquad (4)$$

The values for the upper and lower control levels ($\chi^2{}_u$ and $\chi^2{}_l$) may be taken from statistical tables. More details about the estimation of a standard deviation may be found in statistical publications (see [34] to [37]).

3.2 For blended fertilizer, a practical method is given in [38]. The method can be used to evaluate how well a given mixer blends the components used in the blending process. By carrying out the procedure for various mixing times it is possible to determine the optimum mixing time.

It is recommended to take at least ten samples at equally spaced intervals during the discharge of the mixer. The samples are collected in separate containers and then analysed separately. The calculated average nutrient content of the blend is compared with the calculated analysis of the stream samples. If the two do not compare closely this points to an equipment problem, such as a scale malfunction or misreading, or a problem in obtaining or analyzing the samples.

3.3 The estimate of the standard deviation (s^2) may be used in different ways as a measure of degree of mixing:

a) it may be compared directly with a given goal ($\sigma^2{}_{goal}$);

b) it may be used to calculate a confidence level for the analytical values themselves and compare this confidence level(s) with given tolerance limits;or

c) to calculate a "mixing index" related to a theoretical standard deviaton before mixing (σ_0) or in the statistical mixture (σ_{st}). Such a mixing index may have the form:

$$M_1 = s^2 / \sigma^2{}_o \qquad\qquad (5)$$

$$M_2 = s^2 / \sigma^2{}_{st} \qquad\qquad (6)$$

or

$$M_3 = \frac{s^2 - \sigma^2{}_o}{\sigma^2{}_o - \sigma^2{}_{st}} \qquad\qquad (7)$$

Mixing indices may be useful in the comparative description of mixers.

If similar materials are used, two or more mixers can be compared by calculating the individual variances to see which mixer has the lowest total variance and, therefore, does the best mixing job.

The same scheme can also be followed with the same mixer but using different mixing times, to determine the optimum mixing time.

3.4 The result of this method is sensitive to the number and masses of the individual samples taken. To compare mixers or mixing-times it is recommended to use the same number and mass of samples.

3.5 To calculate standard-deviation and confidence level, the necessary condition (Gaussian distribution of the analytical nutrient content within the blend) is usually not given. For example, in the case of semi

continuous mixing in a drum-mixer there is a pre-fraction and also a post-fraction, which does not belong to the same distribution as the mid-fraction.

3.6 For control procedures (labelling or mixing quality) this method is too time consuming and also expensive.

3.7 Due to segregation caused by handling of blended fertilizers, measured standard deviations and calculated mixing indices describe a blend only as it is at the time the samples are taken.

4 Identification of bulk blends as such

To identify a bulk blend as such, the measure of degree of mixing is not the appropriate procedure.

Simple blends may be identified as such by visual inspection if the particles are apparently different – even though the differing color of particles not always coincide with a difference in chemical composition.

More sophisticated blends may be identified as such after an analytical investigation of the distribution of some relevant property within the blend – e.g. nutrient content. In some cases the analysis of the nutrient content of a number of individual granules may identify a blend as such. However, the identification of such a blend requires more sophisticated methods, and this will be more time consuming and also costly. However, the existing sampling and analytical methods should be adopted for this specific aim.

5 Indirect methods (SGN, UI, GSI, MQI) for assessing the physical compatibility of raw materials

5.1 General

After they are mixed, the segregation of the mixed material is influenced by the physical properties of the components. The most important of them are particle size, particle density and particle shape. Conversely segregation may be avoided or minimized and the mixing step will give a "good" blend if the physical properties of the components are "compatible" (see [39] to [41]). The most important of these properties is the particle size.

5.2 Size Guide Number (SGN)

One of the simplest methods for assessing the size compatibility of granular components is known as Size Guide Number (SGN) (see [42] to [48]). The Size Guide Number is defined as:

$$SGN = d_{50} \times 100 \tag{8}$$

where

d_{50} is the median particle diameter.

SGN is used as a helpful instrument in the selection of raw materials to be blended. However, because SGN is based on d_{50}, it does not consider the spread of particle sizes.

5.3 Uniformity Index (UI)

A second measure of compatibility of grain size distribution is the Uniformity Index; it defines the ratio of the sizes of small (5 % level) and large particles, (90 % level) expressed in percent:

$$UI = \frac{d_5}{d_{90}} \times 100 \tag{9}$$

The determination of d_5 and d_{90} requires the use of more sieves than are usually included in a normal sieve analysis : to obtain accurate measures of d_5 and d_{90} the sieves must be close to the estimated values for d_5

and d_{90}. Calculations based on linear interpolation tend to underestimate the value for d_5 and overestimate the value for d_{90} with double error in spread measurement.

5.4   Granulometric Spread Index (GSI)

The statistical problems of linear interpolation are minimized when the sieves for fine and coarse are closer to the linear part of the distribution curve, for example for d_{16} and d_{84}. In the Gaussian distribution d_{84} - d_{16} is 2s, so the average size range variation coefficient or Granulometric Spread Index (GSI) is given by:

$$\text{GSI} = \left([d_{84} - d_{16}]/(2 \times d_{50})\right) \times 100 \tag{10}$$

5.5   The Mixing Quality Index (MQI)

MQI is calculated from the variation coefficients of SGN_s and UI_s between the individual materials to be blended (see [49] and [50]):

MQI = 1 - CV of SGN_s - CV of UI_s   (11)

5.6   Other physical properties

It may be reasonable to use grain density to evaluate the limits for compatibility of components to be mixed. In most commercial cases, the components of a blend have similiar densities with exception of urea. The combination of size and density to calculate an overall quality index and to "balance" different influences to achieve blend quality has not yet been achieved.

The indirect methods, SGN, UI, GSI, and MQI, to check the compatibility of grain size distribution of the components of a blend are helpful in the selection of the components; they cannot be used as control instruments for labelling or to evaluate the quality of finished blends, mixers or to determine the optimum mixing time.

5.7   French standard NF U42-405

In this method, the fertilizer is split in three fractions with a combination of sieves for both: "fines" and "coarse". If the top (oversize) or the bottom (fines) contains more than 10 % of the sample, the oversize and undersize will be analysed chemically for their nutrient content (N, P_2O_5 , K_2O, MgO etc.). If the results of the "fines" and the "oversize" are close to the declared contents, the fertilizer is regarded as homogeneous, so an ideal blend with physically similar components cannot be identified as a blend. The sieving step destroys the degree of mixing of the bulk, breaking it down into sieve-fractions. The method works even when the product has not been mixed. So the test may be regarded as an a posteriori test for compatibility of the components used.

6   Conclusion

6.1   Visual inspection may identify simple blends but more sophisticated blends may be recognized as such only after an analytical investigation of the distribution of a specific property within the bulk.

6.2   While a mean value of a distribution does not contain any information about degree of mixing, the standard deviation or coefficient of variation may be such a measure. The direct method to determine the standard deviation as a measure of degree of mixing is time consuming and expensive. This method may be used only for specific purposes, e.g. to compare mixers or optimize the mixing time.

6.3   Indirect methods (SGN, UI, GSI, MQI etc.) control the compatibility of the components of the blend but cannot control the labelling of a blend or the quality of the mix itself.

6.4   The French standard NF U 42-405 also indirectly controls the compatibility of the components used but not the labelling of a blend or the effectiveness of the mixing procedure.

6.5   Degree of mixing is not a permanent property of a blend : segregation caused by handling may change the "degree of mixing" of the blend.