GUIDANCE FOR SAFE HANDLING AND UTILIZATION OF NON-CONFORMING SOLID FERTILIZERS AND RELATED MATERIALS FOR FERTILIZER IMPORTERS, DISTRIBUTORS AND MERCHANTS



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1. INTRODUCTION

This guidance is intended for fertilizer importers, distributors and merchants. It concerns the safe management of solid non-conforming (i.e. off-spec and reject) fertilizer products (with particular attention to ammonium nitrate based materials) and associated raw materials. During storage and in the handling activities, fines, deteriorated and contaminated materials may be generated, some of which can be potentially more hazardous than the standard products and, therefore, need to be carefully managed.

This guidance offers alternative options, which the importers, distributors and merchants should evaluate in relation to their own particular situation and select the most suitable one having carried out a risk assessment. Some options may be 'contracted out' to fertilizer producers or other similar organisations that may have the required facilities. Similarly, expert advice, where appropriate, should be sought from producers when carrying out a risk assessment. It should also be noted that some products may not be sold as EC fertilizers and, therefore, may not display adequate information on the packages as to their nitrogen source material. In such cases expert advice should be obtained from the suppliers.

It must be noted that national legislation takes precedence over the guidance given in this document.



2. GENERAL GUIDANCE, BASIC PRINCIPLES AND DEFINITIONS

2.1. General Guidance and Basic Principles

In the fertilizer business, importers and distributors typically store and handle a number of products and other materials and these operations can generate non-conforming materials, either as off-spec or reject materials.

Various methods are theoretically possible for the safe utilization of the non-conforming materials, depending on the extent and nature of the deviation or degradation. These methods are reviewed for various types of AN based products, urea-based products and a range of other agricultural materials.

Most international classification systems specify a maximum limit of 0.2% for combustible material (expressed as carbon) in Ammonium Nitrate which is classified as an oxidizer, e.g. class 5.1 in the UN transport scheme. If this limit is exceeded the material falls into the explosives class.

As the general principles of a safety management system, the importers, distributors and merchants should use the best practices outlined below. Strict adherence to these principles is recommended, particularly where the materials are handled in bulk.

- i Minimise the potential for the generation of non-conforming materials as a high priority.
- ii Ensure schemes, supported by written procedures, are in place for the handling and treatment of these materials.
- iii Take care to minimise the quantities of rejects accumulated and the period for which they are held. Follow the principle of firstin-first-out as far as is practicable. Where necessary, promptly dilute rejects to render them safe.
- iv Keep floors clean, avoiding the accumulation of deposits of fertilizer materials. Avoid the use of organic materials such as sawdust for floor drying purposes.
- v Keep non-conforming materials separated from sound products and do not mix different types without a prior risk assessment.
- vi Take care with materials returned from customers because of the possibility of contamination.
- vii Where reject or off-spec material is treated or diluted to render it safe prior to sale, or where it is suitable for sale in its own right, it must conform to the relevant national legislation.
- viii Where relevant, make importers, distributors and merchants aware of the potential hazards of ammonium nitrate based fertilizers and give them appropriate training.
- ix Never use explosives to break up caked fertilizer.
- x Carry out all procedures to render material safe with due care and attention to safety. Take care also to avoid contaminating watercourses.

2.2. Definitions

■ Non-conforming fertilizer materials

Non-conforming materials are those materials which do not meet the characteristics of the intended products at the time of storage or when marketed. They include both off-spec and reject materials, which are defined below. Essentially, they include everything other than marketable specified product.

Off-spec products

A number of safety and quality related characteristics are specified for fertilizers. Examples are: the nutrient content; moisture level; particle size; pH; presence of proscriptive concentrations of heavy metals, chloride and carbon; bulk density; oil retention (porosity); detonability and the capability of self-sustaining decomposition.

Changes in one or more of these characteristics can occur during storage and subsequent handling, taking the product out of specification due to, for example, moisture pick-up, physical breakdown, caking and contamination. The resulting materials are defined as off-spec materials in this guidance.

Most of such changes have no significant impact on the safety of the products but they tend to give rise to quality issues.

Reject materials

Reject materials are those non-conforming materials which are out of specification, or which have deteriorated during storage and/or handling to such an extent that they can be considered potentially hazardous. They cannot be sold as fertilizer products and may require treatment to render them safe.

Examples include: those which contain more than the maximum permitted level of combustible material; those which have physically degraded into fines and could fail the Detonation Resistance Test and product grossly contaminated with reactive substances.

Ammonium Nitrate based fertilizers

Fertilizers containing nitrogen (N) in both ammonium (NH $_{4+})$ and nitrate (NO $_3$) forms.

Self-sustaining decomposition (SSD)

Decomposition in fertilizers, initiated by an external heat source, that continues even when the heat source is removed (See Appendix 1).



3. MATERIALS

These include fertilizers, typical raw materials and other products, which may be stored in the facility and can be potential sources of contamination, e.g. seeds, pesticides, animal feed and agricultural products.

Fertilizers currently marketed in Europe are detailed in the European Regulation (EC) No. 2003/2003. Other products may be possible depending on national regulations. The main types of fertilizers currently marketed in Europe include:

- Ammonium nitrate (AN)
- Calcium ammonium nitrate (CAN)
- Urea
- Compound fertilizers (e.g. NP, NK and NPK)
- Sulphate-containing fertilizers such as ammonium sulphate (AS), ammonium sulphate nitrate (ASN) and mixtures of AN with calcium sulphate.

- Phosphate fertilizers such as mono ammonium phosphate (MAP), di ammonium phosphate (DAP), single super phosphate (SSP) and triple super phosphate (TSP)
- Potassium-containing fertilizers such as potassium nitrate (NOP), potassium chloride (MOP) and potassium sulphate (SOP).

Other materials

■ Various agricultural products (see above) and raw materials such as limestone, dolomite, magnesite, phosphate rock, gypsum, calcium sulphate, anhydrite, sand and clay.



4. GENERATION OF NON-CONFORMING MATERIALS AND TREATMENT OPTIONS

4.1. Typical, Relevant Activities

Sound products can become non-conforming materials during various activities, for example:

- Physically breaking down into fines during handling or storage under poor conditions,
- Contamination with other materials, spillages due to failure of equipment or spillages from damaged bags
- Moisture ingress,
- Maintenance-related activities, requiring the removal of deposits and scales of fertilizer materials from equipment,
- Caking leading to the formation of lumps.

4.2. Practical Options

A number of practical methods are available for utilizing off-spec and reject materials as described below.

Repackaging, reworking and blending: Clean spilled products, or those with minor deviations from the standard, can be repackaged directly or 'reworked'. This may involve simple physical operations such as screening, mixing and bagging. Blending simply involves mixing with good product.

Selling as product with different specification or application: Offspec materials with minor deviations such as those relating to size, appearance or caking tendency can be sold, for example, as off-spec products or as raw materials for the manufacture of blends/NPK fertilizers or other products.

Return to supplier or manufacturer: This may be an option depending on the distances involved and any commercial arrangements.

Dissolving to form aqueous solution: Solid non-conforming materials can be conveniently dissolved to generate aqueous solutions, if necessary by outsourcing the processing work. Depending on the purity, concentration and similar factors, such solutions can be sold as fluid fertilizers or to fertilizer producers for use in the manufacturing process.

Dilution with fillers (inert materials): Reject materials, particularly those based on AN, which are potentially hazardous and cannot be readily treated by any of the above methods in a safe manner, can be rendered safe by dilution with non-reactive diluents (see below). It may be necessary to contract out this work, e.g. to manufacturers with the required expertise or to other third parties.

A dilution ratio of 1:1 by weight is recommended, based on work done with AN fines and the practical simplicity of the process (Ref. 1-3). This work shows that limestone, china clay, dolomite, gypsum, phosphate rock, sand and magnesium oxide are safe and effective diluents when considering detonation sensitivity. Care should be taken to see that they are not in the form of caked lumps or of incompatible size. Fertilizer materials such as MAP, DAP, SSP and TSP do not appear to have an effective desensitising effect and, therefore, they are not recommended as diluents. The selection of dilution ratios other than 1:1 should be based on a risk assessment. The treated material can be sold or utilized in blending following risk assessments. Mixing AN fines with NP, NK and NPK fines should be avoided since chloride, for instance, can enhance the sensitivity of AN. This may be permitted when justifications are based on a risk assessment.



5. DETAILED GUIDANCE

5.1. Ammonium Nitrate Based Fertilizers

5.1.1. Fines and Dust

Where the level of fines takes the product outside the specified or applicable legal limits, it may be possible to sell it as an off-spec product. Alternatively, it can be screened to remove fines.

5.1.2. Returns from Storage, Loading Departments and Dedicated Areas

Such returns mainly comprise fines and coarse material from screening operations.

Store screened fines in loading departments or dedicated areas. Maximum quantities of each product type, shall be defined and documented. The dedicated areas shall be inspected regularly and the storage cleared at least once every 3 months.

Store returns of AN, high N straight and compound (NPK, NK and NP) fertilizers, CAN, ASN and urea separately from each other in order to avoid cross-contamination.

Treatment options:

Dissolve to form a solution or dilute with suitable inert materials in ratio 1:1, unless a risk assessment allows a different ratio.

Contaminated materials: see Section 5.1.6.

5.1.3. Returns from Farmers and Other Customers

Returns from these sources comprise, in the main, deteriorated product from within the distribution chain and from the end user. In practice, this is usually due to water ingress or caking. However, it can also include damaged bags containing good product, which are covered in the next section. In operations involving loose bulk products, deteriorated products are generally not returned to the suppliers, who give appropriate advice to those in the distribution chain as to the actions to take, such as selling as off-spec, reworking or utilizing in making blends. In abnormal situations, contaminated product, fines or oversize material may be returned in packaged or bulk form. Only those products, which can be traced back to the supplier in a reliable way, should be accepted as returns.

- Keep records of the returned materials, e.g. name of company returning, type of product, quantity, date and reason.
- Check whether product is contaminated. If contaminated, identify the nature of the contamination and, treat accordingly, following a risk assessment (see Section 5.1.6).
- Where necessary and practicable, screen out good product and treat the remainder. Rework in a manner appropriate to the material, as described in Section 4.2.

5.1.4. Good (i.e. Standard) Product in Damaged Bags

■ Check to confirm the product is good.

Temporarily seal the bags to protect the product and re-bag as soon as possible.

5.1.5. Spilled Material

Clean Spillages

Clean spillages from split bags, conveyers, hoppers and elevators can be collected and repackaged or reworked, provided the product is not contaminated by other materials, floor debris, oil/grease etc.

<u>Contaminated Spillages</u> See Section 5.1.6.

5.1.6. Contaminated Material (Including Cross-contamination) The various ways in which fertilizers can become contaminated are considered below.

The inventories of all contaminated materials should be kept to a minimum; they should not be allowed to accumulate. Large quantities should be kept in bags.

Contamination of product, particularly of spilled product, with nonfertilizer material: e.g. wood, sand, plastic, rubber, seeds, animal feed and sawdust, or even with organic fertilizer.

Recommendations for utilization include:

- Sell with precautionary safety conditions following a risk assessment.
- If possible, remove the contamination and repackage/rework.
- Where appropriate, dilute with suitable material in a ratio of 1:1 unless a risk assessment allows a different ratio. Seek expert advice from the manufacturer/supplier if in doubt.

Mixing with oil, grease, etc

This refers to dirty spillages, which may be contaminated with oil or grease, and are usually damp or wet.

Options for disposal include:

- Rework/blend if safe to do so based on risk assessment.
- Dissolve and dispose of or sell as a solution depending on the quantities involved.
- Dilute and/or dispose of as a waste material using authorised waste handling procedures, particularly when it is heavily contaminated.

Contamination with non-fertilizer chemicals

The risk depends on the nature of the contaminant. If the mixture can be predicted to be non-hazardous, sell or rework. Otherwise, carry out a risk assessment; if necessary contact the suppliers of the fertilizer and chemicals for information about the contaminant and carry out the recommended action based on their conclusions.

Mixing with floor sweepings

Floor sweepings can contain various materials such as fertilizers, raw materials, floor coverings and/or rubber. Options for disposal or utilization include:

- Selling with precautionary safety conditions following a risk assessment.
- Dissolving, filtering and selling as a solution.
- Disposing of as a waste material using authorised procedures.

Cross-contamination with other fertilizers, e.g. from adjoining bulk bays.

Avoid accidental and/or potentially hazardous mixing of different types of fertilizer.

- Seek advice ideally from the manufacturers/suppliers or, failing that from other sources.
- Carry out a risk assessment taking into consideration various safety aspects such as the AN content and the properties of the contaminants. Options for treatment include selling in a controlled way, reworking, blending or diluting.

5.1.7. Build-up and Deposits on Equipment

Materials can collect on and around conveying equipment, fork lift trucks and packaging equipment. These materials are generally similar to the normal products in composition terms and are therefore best reworked or utilized in other ways.

5.2. Urea and Urea-based Fertilizers

Urea is non-hazardous in nature, other than when involved in a fire. Therefore, fines, wet product, etc., do not generally affect safety.

Avoid contamination of AN with urea in solid form, as urea can enhance the detonation hazard of AN.

A solution of Urea and AN (UAN) is widely used as a liquid fertilizer and is not classified as hazardous. However, under certain conditions the solution may become concentrated and solids may separate out which, if wrongly treated, can be hazardous.

Urea-based NPKs are also non-hazardous other than in a fire.

Contamination with nitric acid could lead to the formation of ureanitrate, which is shock sensitive in nature and can thus give rise to a detonation hazard; if this is suspected seek expert advice.

5.3. Other Materials

5.3.1. Ammonium Sulphate

AS does not present a fire or explosion hazard on its own. As explained in Appendix 1, it can form hazardous mixtures with AN. Take appropriate precautions as outlined in Appendix 1.

5.3.2. MAP and DAP (NP Fertilizers), TSP, SSP, Potash (KCl)

These materials are non-hazardous by themselves and are widely used in NPK production. However, they are not efficient for reducing the sensitivity towards detonation from AN fines/dust and, therefore, their use as a diluent to render AN rejects safe should be avoided (Ref. 3).

5.3.3. Potassium Nitrate (NK Fertilizer, NOP)

Potassium Nitrate is an oxidizer and, as such, needs to be kept away from combustible materials. Avoid inadvertent mixing with AN-based fertilizers as this will increase the nitrate level, and this could result in enhanced sensitivity of the mixture in terms of potential decomposition, fire and explosion hazards. On its own, it does not present a detonation hazard and in this respect fines are not a safety hazard.

5.3.4. Potassium Sulphate

Potassium Sulphate is non-hazardous and widely used in NPK production. It can be used as a component in NPK fertilizers to reduce the potential for SSD.

5.3.5. Limestone, Dolomite, Magnesite, Phosphate Rock, Gypsum, Calcium Sulphate, Anhydrite, Sand and Clay

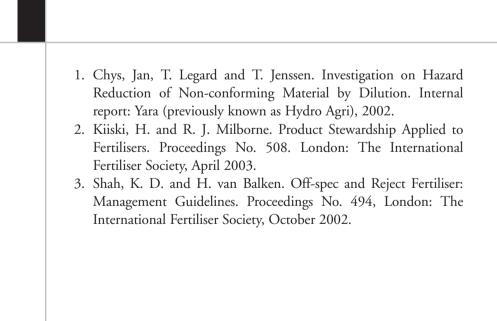
These materials are non-hazardous by themselves and can be used to dilute reject material. No special precautions are necessary.

5.3.6. Calcium Nitrate Fertilizer

The commercial grade of calcium nitrate fertilizer is non-hazardous when it consists mainly of a double salt (calcium nitrate and ammonium nitrate) and contains not more than 10% of ammonium nitrate with at least 12% water of crystallisation [See provision 208 of the U.N. Orange book]. Material not conforming to these criteria is classified as an oxidizer and shall be handled accordingly. Fines of the fertilizer grade are not hazardous.



6. REFERENCES



APPENDIX 1

Potential Hazards

The three main potential chemical hazards of relevance concerning AN based materials are:

- (i) Fire.
- (ii) Decomposition (including self-sustaining decomposition).
- (iii) Explosion: e.g. detonation.

The affecting factors are briefly discussed here.

Ammonium nitrate is an oxidizing substance and can therefore provide oxygen in the absence of air. However, **ammonium nitrate itself does not burn**. Fire hazard can increase if the nitrate based products, particularly spillages, are contaminated with combustible materials – sawdust is sometimes used as a drying agent on wet floors. In a fire situation ammonium nitrate can give off toxic fumes such as NO₂.

Ammonium nitrate undergoes thermal decomposition by means of a number of reactions when heated well above its melting point (169°C). Some of the product gases are toxic in nature, for example NO_2 . The onset temperature can reduce and the rate of decomposition is enhanced by a number of sensitising materials. Sensitising materials can be:

- (i) Acids, chromates, chlorinated chemicals and various metals such as zinc and copper and their salts.
- (ii) Other substances on those sites which produce a range of chemical products.
- (iii) Contaminants during transport and/or storage.
- (iv) Products returned from customers.
- (v) Mixtures of NPK fertilizer products or their dust.

Owing to the nature of ammonium nitrate, contaminants must be avoided.

As described above, both fire and decomposition can lead to the evolution of toxic gases.

All AN based fertilizers are produced to have a high resistance to detonation; they pass the EU Detonation Resistance Test (Regulation EC No. 2003/2003, Annex III.4). The sensitivity to detonation of these products can, however, increase due to a substantial reduction in particle size; to an increase in porosity (hence a decrease in bulk density); to physical characteristics of additives or an increase in the levels (above safe limits) of combustible materials; and also due to organic and other sensitising materials such as copper and chloride. Thus, fines or dust can be more sensitive than the standard product (Ref. 3). It is worth noting that in processes where an organic coating is applied to products, fines may take up relatively more coating agent, thus enhancing their sensitivity. The addition of AS within certain limits can increase the sensitivity to detonation and SSD.

Since various factors such as those mentioned above can affect the detonation behaviour, it is not possible to rely exclusively on the chemical composition (in terms of AN content).



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