



2005 IFA TECHNICAL COMMITTEE MEETING

11-13 April 2005, Alexandria, Egypt

Technical Research Paper no. 2

**Enhancing the Efficiency of Urea and
Ammonium Nitrate by the Addition
of Other Nutrients**

presented by

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About the IFA Technical Committee

The IFA Technical Committee encourages the development and adoption of technology improvements that can lead to greater production efficiencies and reduced emissions, as well as better health and safety standards throughout the fertilizer industry. Our mission is to actively promote the sustainable development of efficient and responsible production, storage and transportation of all plant nutrients. The Technical Committee accomplishes these objectives through a variety of channels, including:

- Technical and policy-oriented information materials. The committee regularly conducts surveys and produces reports on key industry metrics, including the IFA Energy Efficiency and CO₂ Emissions Report, the IFA Safety Report, and the IFA Emissions Report. This work enables member companies to assess their operations over time, make comparisons with similar facilities on an established level of performance, determine the need for technology improvements and identify good industrial and management practices.
- Regular exchange of information on technology developments and industrial practices. A key role of the IFA Technical Committee is to encourage ongoing technical innovation in the fertilizer industry through the development, compilation and exchange of technical information between members, researchers, engineers, equipment suppliers and other industry associations. To this end, the committee organizes a Technical Symposium every other year to examine progress in the production technology of fertilizers. Each Symposium traditionally features the presentation of 30-40 new technical papers from member companies worldwide, providing members with information on the latest technological developments. In the intervening years, the committee holds a variety of meetings to assess current industrial practices and standards, with an eye toward identifying key developments of interest to members.
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Enhancing the Efficiency of Urea and Ammonium Nitrate by the Addition of Other Nutrients

Abstract

Plant Nutrients

- Crops need a number of mineral elements for healthy growth.
- The generally accepted number of essential nutrients required is 20, which includes carbon, hydrogen and oxygen as well as 17 other mineral elements which are nitrogen, phosphorous, potassium, calcium, magnesium, sulphur, boron, chlorine, copper, iron, manganese, molybdenum, zinc, silicon, sodium, cobalt, and vanadium.
- These elements are divided into three groups; Primary Nutrients (nitrogen, phosphorous, potassium), Secondary Nutrients (calcium, magnesium, sulphur), and Micro-Nutrients (the rest).

Abu Qir Production with Other Nutrients

Abu Qir Fertilizer Company planned to produce urea and ammonium nitrate with various secondary and micronutrients. The aims of this planning were:

1. Improving the chemical properties of urea and ammonium nitrate to give all the types of crops the required nutrients needed to good growth and high productivities and to avoid symptoms of nutrients deficiency.
2. Improving the physical properties which means decreasing its solubility in soil, which thus means avoiding losses of fertilizers and escape deeply in soil away from the plant roots.
3. Achieving fertilizers balancing in the soils by providing it with different types of nutrients.

The main secondary and micro nutrients selected to be added to urea and ammonium nitrate depend on its relevant importance for the plant growth.

These nutrients are:

- Magnesium and sulphur as secondary nutrients.
- Iron, manganese, zinc as the main important micro nutrients.

The main essential requirement for the addition of these nutrients is its addition in the soluble and ionized form to be absorbed by the plants.

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All papers and presentations prepared for the IFA Technical Committee Meeting in Alexandria will be compiled on a cd-rom to be released in May 2005.

1- Introduction

1.A) Plant Nutrients

- The crops need a number of mineral elements for healthy growth.
- The generally accepted number of essential nutrients required is 20, which includes carbon, hydrogen and oxygen as well as 17 other mineral elements which are nitrogen, phosphorous, potassium, calcium, magnesium, sulphur, boron, chlorine, copper, iron, manganese, molybdenum, zinc, silicon, sodium, cobalt, and vanadium.
- Some of the previous elements in addition to some other elements are found in the plant but their essentiality hasn't been determined yet. Examples of these elements are; aluminum, arsenic, barium, bromine, cobalt, fluorine, iodine, lithium, selenium, silicon, sodium, strontium, titanium, vanadium, and cobalt.
- Carbon, hydrogen, and oxygen are taken from the air and the water. The other elements are divided into three groups; **Primary Nutrients** (nitrogen, phosphorous, and potassium), **Secondary Nutrients** (calcium, magnesium, and sulphur), and **Micro-Nutrients** (the rest). All these groups are highly important for the plant growth and are equally essential, regardless of the amounts required.
- The other classification of essential elements are:
 - **Macro – Nutrients**, which include carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, and sulphur.
 - **Micro – Nutrients**, which include iron, zinc, manganese, copper, boron, molybdenum, chlorine, silicon, sodium, cobalt, and vanadium.

1.B) Abu Qir Production with Other Nutrients

In Abu Qir Fertilizer Company a unique planning was implemented to produce urea and ammonium nitrate with various secondary and micronutrients. The aims of this planning were:

- 1- Improving the chemical properties of urea and ammonium nitrate to give all the types of crops the required nutrients needed to good growth and high productivities and to avoid symptoms of nutrients deficiency.
- 2- Improving the physical (mechanical) properties which means producing slow release urea, in other words decreasing its solubility in soil, which means avoiding losses of fertilizers and escape deeply in soil away from the plant roots.
- 3- Achieving fertilizers balancing in the soils by providing it with different types of nutrients.

So Abu Qir succeeded in changing its production structure to fulfill the above mentioned requirements by producing few types of urea each provided with one or more nutrients (secondary or micronutrients), producing ammonium nitrate sustained by seven secondary and micronutrients. Also Abu Qir succeeded to improve the fertilization (fertigation) properties by adding some secondary and micronutrients.

Primary plant nutrient taken from urea as fertilizers, the urea is the main resource of nitrogen to the soil since the pure urea contains 46.57 nitrogen, and ammonium nitrate that is produced with different grades such as 33.5% N₂, 31% N₂, and other types of ammonium nitrate containing fertilizers.

2- Urea

Urea is the main direct fertilizer source of nitrogen, where nitrogen composes 46.5% of its contents.

2.A) Nitrogen

The nitrogen is taken up by plants primarily as nitrate (NO_3^-) or as ammonium ions (NH_4^+).

Plants can utilize both of these forms of nitrogen in their growth process.

Most of the nitrogen is taken up by the plants in the nitrate form due to the following two reasons:

- 1- Nitrogen from nitrate is mobile in the soil and moves with soil water to plant roots.
- 2- All forms of nitrogen fertilizer added to soils are changed to nitrate under proper conditions of temperature, aeration and moisture by the soil organism.

2.A.1) Importance of Nitrogen

A) Nitrogen is utilized by plants to synthesize amino acids, which in turn form proteins.

B) Nitrogen is also required by plants for other vital compounds such as chlorophyll, nucleic acids, and enzymes.

2.A.2) Symptoms of nitrogen deficiency in plants include:

A) Slow growth, stunting.

B) Yellow green color (chlorosis).

C) Firing of tips and margins of leaves beginning with more mature leaves.

2.B) Urea Plus Other Nutrients

- Urea provided by sulphur (Urea sulphate).
- Urea provided by magnesium and sulphur (Urea magnesium sulphate).
- Urea provided by zinc and sulphur (Urea zinc sulphate).
- Urea provided with manganese sulphate).
- Urea – multi-nutrients (Urea provided with magnesium, sulphur, manganese, zinc, and boron).

N.B.: Abu Qir is currently producing the first three types.

2.B.1) Secondary Nutrients added to Urea

1.a) Magnesium

1.a.1) Forms of Magnesium Absorbed by Plants

Magnesium is up taken by the plant in the form of the magnesium ions (Mg^{++}).

1.a.2) Importance and Uses of Magnesium

Magnesium is essential for the photosynthesis process because the chlorophyll molecule contains magnesium.

Magnesium serves as an activator for many plant enzymes required in the growth process.

Magnesium ions are mobile within plant tissues and can be translocated from older to younger tissues under condition of deficiency.

The most common use of magnesium fertilizers has been for celery and citrus.

1.a.3) Symptoms of magnesium deficiency

- Interviental chlorosis (yellowing) in older leaves.
- Curling of leaves upward along margins.
- Marginal yellowing with green area along mid-rib.

1.b) Sulphur

1.b.1) Form of sulphur absorbed by plants

- The sulphate is up taken by plants in the form of sulphate ion (SO_4^-).
- The sulphur can be also absorbed from air through leaves in the area where the atmosphere is rich of sulphur compound.

1.b.2) Importance of the sulphur for the plants

- Sulphur is a constituent of three amino-acids (cystine, methionine, and cysteine) therefore it is essential for protein synthesis.
- It is essential for nodule formation on legume roots.
- It is responsible for the characteristics odors of some plants such as garlic and onions.

1.b.3) Symptoms of sulphur deficiency in plants

- Young leaves light-green to yellowish color, in some plants it affect older tissues.
- Small and spindly plants.
- Retarded growth rate and delay maturity.

2.B.2) Micro – nutrients – added to Urea

2.a) Zinc

- Zinc is one of the main micronutrients can be added to urea.

2.a.1) The form of Zinc absorbed by plants

- The more important source of zinc which can be added to urea is the zinc sulphate.
- Zinc is up taken by plants as zinc ion , where zinc sulphate is ionized in soils to zinc ion Zn^{++} plus sulphate ion SO_4^- .

2.a.2) The importance of zinc to plants

- Zinc is essential constituent of several important enzyme system in plants.
- It controls the synthesis of indoleacetic acid.
- Plant growth regulator
- Many crops require zinc fertilization such as tree fruits, nuts, grapes, beans, onions, tomatoes, cotton , rice and corn.

2.a.3) Symptoms of zinc deficiency in the plant

- Decrease in stem length and rustling of terminal leaves.
- Reduced fruit bud formation.
- Mottled leaves (interviental chlorosis).
- Dieback of twigs after first year.

3) Production of Urea Ammonium Sulphate

3.A) Ammonium Sulphate (NH₄)₂ SO₃.H₂O

- Urea ammonium sulphate is produced by the addition of ammonium sulphate to urea with required ratio according to the market request.
- It can be produced by addition of ammonium sulphate up to 28% which means sulphur content of about 7%.
- Due to market request AFC produced urea with ammonium sulphate between 0.8 - 1 %.
- Ammonium sulphate itself is considered one of the oldest forms of nitrogen fertilizer since it contains primary nutrients which are nitrogen and secondary nutrients which is sulphur.
- It refers to ammonium sulphate as 21-0-0-24.5 where it contains 21 percent nitrogen and 24% sulphur.
- The ammonium nitrate is completely soluble at 100°C, so it is easy to dissolve it in hot condensate at 100°C and add it to urea solution 80% before introducing it to the final evaporation in the granulation plant.

3.B) Process Description (see flow diagram number (1))

- Ammonium sulphate can be add at low concentration to a concentrated solution after final evaporation before introducing it directly to granulator.
- In the case where it is introduced directly to the granulator it can lead to the formation of dust, however if it is introduced with liquid urea to evaporation and then to the granulator, dust formation is completely eliminated.
- The ammonium sulphate which is in crystals form is dissolved in hot condensate at 100°C in the preparation tank provided with agitator or with circulation pump to help in the dissolution of the crystals (agitator is better)
- The tank is provided by local level indicator.
- The tank capacity can be varied according to the production capacity and concentration of ammonium sulphate to be added.
- The tank should be manufactured from stainless steel 304 or 304 L.
- The preparation tank should be thermally insulated.
- After complete dissolution the solution is transferred from preparation tank to feeding (dosing) tank by means of transfer pump which may be used as circulation pump also.
- The feeding tank is manufactured from stainless steel 304 or 304 L and thermally isolated.
- The feeding tank is provided by level indicator connected to DCS system.
- The AS solution is fed to the suction of urea solution (80%) pump from storage tank to final evaporator through the AS solution feed (injection) pump.
- Flow indicator connected to DCS is provided on the discharge of AS solution feed pump.
- Better controlling can be obtained by installing automatic flow control valve on the discharge line of AS solution feed pump.
- Preparation and feed tanks can be provided by temperature indicator connected to the DCS system.

3.C) Problems Faced

3.C.1) Addition of ammonium sulphate

The main important parameters to be concerned during manufacturing were to keep the hardness and screen analysis at the required value.

Ammonium sulphate dissolved in urea solution as described before and injected directly to concentrated solution outlet final evaporator (96%) to granulator.

The urea formaldehyde which added at rate of 0.55% weight as anti-caking was decreased to 0.3%.

The following changes were observed

* The urea production rate was decreased from 85 mt/h to 63 mt/h as a result of dust formation and increase undersize and fines inside granulator.

* Screen distribution (analysis) of required size 2 - 4.5 mm was decreased from 98% to 63% weight.

* Increase dust formation inside granulator and fluidized bed coolers.

* Continuous blockage of fluidization perforated plate inside granulator and fluidized bed coolers which affect the temperature of product inside of this equipment.

These changes happened just half an hour after decreasing the urea formaldehyde flow rate from 0.55% to 0.3 %.

All these changes led to stopping the granulation unit to clean and flush the granulators, coolers, ducts, chutes, etc.

3.C.2) Results of problem happened

The above problems indicated that the ammonium sulphate can not be used mainly to improve the physical properties, but it can be used as a source of sulphur as secondary nutrients.

So the addition of urea formaldehyde is very essential at higher rate when ammonium sulphate added to urea as source of sulphur.

3.C.3) The steps taken to solve the problem

- Using urea formaldehyde at a rate between 0.55 – 0.6 % weight.

- Increase temperature inside granulator from 106C to 110C.

- Increase the temperature of concentrated solution from evaporator to granulator from 132°C to 135°C.

- Continuous flow up for the density of solution outlet granulator scrubber and cooler scrubber to detect the quantity of dust going in with fluidization air used in these equipment.

- Cleaning the product screens two times per shift to avoid any leakage and avoid consequent change in product quality.

- Continuous cleaning of the de-dusting system.

- The production of urea sulphate was restarted, where too many improvements occurred, but we still have to modify further steps for further improvement.

- To reach better results, steam condensate was used to dissolve ammonium sulphate.
- The solubility of ammonium sulphate in hot condensate was very good so this solution can be mixed well with concentrated urea from final evaporator directed to granulator.
- Product of urea sulphate started with this procedure almost trouble free and with normal known physical properties.

3.C.4) Improving the quality of the produced urea sulphate

- In addition to the achieved objectives from the addition of sulphur as a secondary nutrient to urea, we are also aiming to improve the physical properties of the urea – sulphate.
- The following modifications were implemented to achieve this target.
- * Instead of injecting urea to the concentrated urea solution outlet evaporator directly to the granulator, we decided after investigation to introduce ammonium sulphate dissolved in hot condensate to urea solution of 80% concentration before introducing to final evaporation. This step gave more flexibility for better mixing of both urea and ammonium sulphate solution and the results were:
 - Completely trouble free operation.
 - Dust free production, which appears also from density measurement of scrubbing solution in both granulator and cooler scrubber.
 - Better improvements in hardness.
 - Moisture content (free) decrease to limit between 0.23 – 0.24 instead of limit between 2.6 – 2.8.
 - Spherity of granules improved.

3.D) Inspection results of evaporation section after one and half year from the production of urea – sulphate

During the annual shutdown of Abu Qir plant (3) in September 2004, it was decided to inspect the tubes of the final evaporator to investigate any troubles from using ammonium sulphate with urea solution concentrated in the heater.

The inspection was done by the urea solution plant Licensor StamiCarbon, where the results were excellent as there was no effect of the sulphate on the tubes, the tubes thickness was the same as the new heater.

4) Production of the urea magnesium sulphate

4.A) Why Urea – Magnesium Sulphate?

As mentioned before, magnesium and sulphur are the two of three of secondary nutrients , where the third is calcium.

The aims of addition of magnesium sulphate to urea are:

- Improving the nutrient efficiency of urea by adding these two important secondary elements.

- Improving the physical properties, where it appears from investigations and preliminary tests that addition of magnesium sulphate to urea will increase the hardness and strength of urea as a result of the bond formation to limit close to 5.6 – 6 kg, which decreases the solubility of urea in soil and prevents losses of nitrogen and permits of the plant to take up of its benefit over long period (i.e., slow release urea). On the other hand this also can decrease the rate of using urea per plant which means economic saving.

4.B) Properties of Magnesium Sulphate

Magnesium sulphate is white hydrous crystals containing seven molecules of water $Mg.SO_4 \cdot 7H_2O$ and its molecular weight is 246.49.

Magnesium sulphate is completely soluble in water at moderate temperature that can facilitate its use and addition to urea solution.

Magnesium sulphate itself is used as fertilizer so when it mixed with urea its added value to the plants will be very high.

The magnesium sulphate salts is commercially known as Epsom (Epsomit).

4.C) Preparation and Addition of Magnesium Sulphate to Urea

4.C.1) Process Description (see process diagram number (2))

- The Magnesium sulphate is prepared and added to urea by the same process of addition of ammonium sulphate.
- The magnesium sulphate (MS) is fed manually or automatically (by belt conveyor) to the preparation tank, where hot condensate can dissolve magnesium sulphate. The tank is provided by agitator or circulation pump to help in dissolving MS.
- After complete dissolving , the solution of MS is transferred to the feed or dozing tank by circulation pump which serves in transfer of MS solution also.
- The solution from feed tank is pumped to the suction of urea solution pump feed to the final evaporator by means of feed pump (one in operation and one stand by).
- Each tank is provided by level indicator and for the feed tank it should be connected to the DCS system.
- Temperature indicator should be provided for each tank, and should be connected to the control room (DCS).
- Two tanks should be made from stainless steel grade 304 or 304 L.
- Both tanks are thermally insulated.
- Flow indicator on the feed line connected to the DCS system is essential for better flow control valve should be provided.

Note : Same unit used for ammonium sulphate preparation and addition can be used for the magnesium sulphate.

4.C.2) Addition steps

Magnesium sulphate solution prepared with the concentration required in the preparation unit as mentioned before.

Feeding with feed pump to the suction of urea solution pump to the concentration unit at the required rate.

4.D) Actions needed to keep the concentration of solution to granulator and moisture in final product at required level

- a) Increase the temperature of solution outlet evaporator (concentration section) from 134°C to 136°C.
- b) Increase temperature of granulator from 107°C to 109°C.

4.E) Problem during manufacturing

Due to physical characters of magnesium sulphate , and binding forces between the particles of urea and magnesium sulphate, the size of granules increased to an un-required limits and overloaded the over size crusher.

4.F) Actions taken to solve the Problems

- a) The temperature of mixed solution from final evaporation was decreased to its original value to be 134°C instead of 136°C.
- b) The level of bed inside granulator was decreased from 50% to 48%.
- c) The temperature of the bed inside the granulator was decreased to its original temperature to be 107°C instead of 109°C.
- d) Decrease the urea formaldehyde flow rate, which is added as an anti caking, to 50% of its value, which means decreasing the formaldehyde in final product from 0.55 % weight to 0.28% weight.

4.G) Final Improvement in the Quality of the Product

In addition of increasing the fertilizer efficiency by addition of two important secondary nutrients the following improvement in physical properties are gained:

- a) Increasing the hardness of the final product to be 5.4 kg instead of 4 kg, due to binding bond and water bridges formed between molecules of urea and magnesium sulphate.
- b) Increasing the granules size and control its increase at required value due to attraction and binding forces between different molecules in the mixtures.
- c) Dust disappeared completely from all the system and that was appeared on the density of scrubbing solution in both granulator and cooler scrubber.
- d) The dust free product means no caking tendency.
- e) Decreasing the urea formaldehyde used by about 50% which means decreasing the production cost.
- f) Decreasing the solubility of urea – magnesium sulphate which decreases the nitrogen losses in the soil and increases its stability and its benefits for the plants over long period.
- g) With avoiding losses of nitrogen in the soil, it also helps in decreasing the injection rate of the fertilizer needed for plants which means saving money for farmers.
- h) The appearance of the product was excellent.
- i) Finally all these properties mean that the urea treated with magnesium sulphate is a slow release urea fertilizer.

5) Production of Urea Zinc – Sulphate

To improve the nutrient balance for soil cultivated in most of Egyptian land which is overloaded by nitrogen, AFC, as mentioned before, is carrying this responsibility and started carrying out this philosophy. So as mentioned before Abu Qir Fertilizer Company succeeded in the production of urea – sulphate and urea magnesium – sulphate. So the third step was to implement the micronutrient to the fertilizers to provide the plants by the most important of them.

5.A) Why Zinc – Sulphate?

As mentioned in section 2.B.2 para 2.a, the zinc is one of the most important micronutrients that can be added to urea, the more important source of zinc that can be added to urea is the zinc sulphate.

The zinc is up taken by plant as zinc ion (Zn^{++}) where zinc sulphate is ionized in the soils to zinc ion (Z^{++}) and sulphate ion (SO_4^{--}).

The importance of the sulphur and zinc for plants are mentioned before.

Zinc is added to the urea in few hundreds < 200 ppm , where it is very important to most of the plants but to some limits.

5.A.1) Properties of Zinc Sulphate

Zinc sulphate is hydrated white crystals containing six water molecules and its molecular weigh is 269.54 $Zn.SO_4.6H_2O$.

Zinc sulphate is completely soluble in water at any degree, for this reason it is suitable to use with urea prills to avoid blockage of prilling device holes (buscket).

5.A.2) Addition of Zinc Sulphate to Urea Prills

2.a) Process description (see process flow diagram (3))

The preparation and addition unit is exactly similar to the unit used in addition of ammonium sulphate and magnesium sulphate to the urea that means that the unit mainly consists of:

- 1- Preparation tank provided with agitator or / and circulation pump.
- 2- Feeding tank where dissolved solution transfer by circulation and transfer pump from preparation tank.
- 3- Each tank is provided with a level indicator, in case of feed tank indicator are connected to control room.
- 4- Solution feed to the suction of the first evaporator feed pump feeding the urea solution at concentration of about 72% by means of injection pump (one in operation and one standby).
- 5- Feed is measured by a flow indicator connected to the control room (DCS system).
- 6- Each tank has a temperature indicator.
- 7- Both tanks are thermally insulated.

2.b) Addition steps:

The zinc sulphate solution added to urea solution at suction of pump feeding urea solution at concentration of about 72% to first evaporator.

The addition and product of urea zinc sulphate was completed free of troubles.

The appearance of product was improved and the quality of urea prills was excellent.

Production of Super Quality – Multi Nutrients Ammonium Nitrate (Modified Ammonium Nitrate)

1) Introduction

Ammonium nitrate is one of the most popular fertilizers and generally is manufactured in forms of prills or granules.

Ammonium nitrate contains a maximum of 35 percent of fixed nitrogen available as plant food.

Some additives are added to ammonium nitrate to improve its quality such as dolomite or limestone which is added as filler to decrease its nitrogen content to the required grade 33.5%, 31%, 27%, etc.

Magnesium nitrate is added to grade 33.5% as a stabilizing agent against thermal degradation at 32.2°C.

Also aluminum sulphate or mixture of aluminum sulphate and ferrous or ferric sulphate are added to ammonium nitrate in some licenses as a stabilizing agent.

Amine dissolved in oil is also added as an anti-caking agent to coat the final product.

In some granulation processes, also granulating agent is added to improve formation of granules inside the granulator.

1.A) Abu Qir Ammonium Nitrate

Abu Qir Fertilizer Company, plant number 2 produces high quality ammonium nitrate granules 33.5% using fluidized bed granulation technology.

This grade contains magnesium nitrate as a stabilizing agent which also increases the fertilization efficiency due to presence of magnesium elements in the soluble form.

In addition to magnesium, calcium present in some limit as calcium nitrate and calcium with magnesium and sulphur are the three secondary nutrients needed for plants.

2) Production of Ammonium Nitrate with Multi-Nutrients

As the ammonium nitrate is an oxidizing agent, and can be subjected to decomposition and evolution of huge quantity of gases in cases where metals or organic compound exist, so the addition of any nutrients or micronutrients to ammonium nitrate should be fully studied, investigated, and carefully selected to avoid any decomposition reaction with ammonium nitrate that can lead to the evolution of huge amounts of gases or can cause explosion.

In most of decomposition reactions, a huge amounts of heat is evolved except in case of decomposition to nitric acid.

For that reason, the decomposition temperature of the ammonium nitrate with any additive should be tested and to be sure that it is far away from the operating conditions, and in the same time, the temperature should be carefully watched in case of any addition to ammonium nitrate to avoid rapid and high increase or decrease in temperature particularly in granulator and concentration section.

3) Nutrients and Micro Nutrients added to Abu Qir Ammonium Nitrate Granules

Taking in consideration that two secondary nutrients exist in ammonium nitrate granules produced in Abu Qir, as mentioned before, which there are magnesium in the form of magnesium nitrate and calcium as calcium nitrate.

By investigation the requirement of the Egyptian agronomist and ministry of agriculture for the nutrients and micro-nutrients needed for the Egyptian crops, it was found that the following nutrients and micronutrients are needed:

- Sulphur as one of the main secondary nutrients (others are magnesium and calcium).
- Iron, zinc and manganese are highly needed.

These elements should be added in the soluble and ionized forms. It was found that the forms which can give these ionized nutrients in the soil to the required ions are sulphate of each, which in the same time will be source of sulphur or sulphate ions.

- Ferrous, zinc, and manganese sulphate are completely soluble in hot condensate.
- The stability of them against decomposition is very high, where its decomposition is between over 250°C to 700°C.
- Laboratory test was done for the three sulphates with ammonium nitrate individually and all together to investigate and detect any decomposition or drop in pH.

3.A) Why these secondary and micro nutrients?

The importance of magnesium, sulphur, and zinc is previously explained, however the importance of iron and manganese is illustrated as follows:

3.A.1) Iron

1.a) Importance of Iron to Plant

Iron is absorbed by plants as Ferrous Ions (Fe^{++}).

- Formation of chlorophyll in plant cells.
- It serves as an activator for biochemical process such as respiration, photosynthesis and symbiotic nitrogen fixation.

1.b) Symptoms of Iron Deficiency

- Interveinal chlorosis of young leaves.
- Twig dieback.
- In severe cases, death of the entire limbs or plants.

1.c) Reasons of Iron Deficiency

- High levels of manganese.
- High lime content in the soil.
- High pH or aeration.

3.A.2) Manganese

2.a) Importance of Manganese to Plant

Manganese is up taken by plants as Manganese Ions (Mn^{++}).

- Manganese is required for the plant as an activator for enzymes in growth processes.
- It assists iron in the chlorophyll formation.

2.b) Use of Manganese

It is used with zinc in the foliar spraying of the commercial citrus.

2.c) Symptoms of Manganese Deficiency

- Interveinal chlorosis of young leaves.
- Gradation of pale-green coloration with darker-color next to veins.

4) Laboratory Tests indicate the following Observation

With manganese sulphate and zinc sulphate, ammonium nitrate is highly stable, no decomposition at temperature $200^{\circ}C$, where the test was done, and no change in the pH. With ferrous sulphate it was observed some little decomposition at temperature above $160^{\circ}C$ and evolution of nitrous oxides and drop in pH of the mixture.

5) Solving decomposition with ferrous sulphate

The main factor that affects the decomposition is the drop in pH to be less than 5.5, so it was required to keep mixture of calculated solution at $pH > 6.5$ small calculated.

By addition of ammonium nitrate to the prepared mixture of three sulphate, and by the addition of some magnesium oxide it was possible to solve this problem completely but magnesium oxide is not completely soluble and cause blockage problem and decrease solubility of ferrous sulphate.

By laboratory test, it was found that increasing the amounts of ammonium nitrate to $2\ m^3$ per each batch of $8\ m^3$ of mixture instead of $1\ m^3$ will control the pH at the required value without addition of any magnesium oxide.

Also to collect the vapour that contains nitrogen oxide in the preparation and feed (dosing) tanks, condenser provided with an ejector driven by steam was installed to collect and condense these vapours and reuse it in the preparation tank.

6) Preparation unit (see flow diagram number (4))

The mixture of the three elements iron, zinc, and manganese sulphate is prepared in unit exactly similar to the unit used in addition of nutrients in urea plant.

The unit consists of:

- Preparation tank provided by agitator or circulation pump to help in the agitation and then transfer of the solution to the feed tank.
- The tank in addition to the feed tank are provided with ejector and condenser to withdraw the vapours, condense it and return it to the tank.
- The tank is provided with a vent directed to a safe height.

- The tank is thermally insulated and provided by level and temperature indicator.
- Feed tank, provided with level and temperature indicator and thermally insulated and connected to ejector and connector.
- Two feed pumps (one in operation and one stand by) to feed the mixtures of three sulphate to the mixing vessel containing the main feed of ammonium nitrate and filler to feed it to the granulator.
- The sulphate feed pumps are provided by flow indicator to adjust the flow to the mixing vessel.
- Electrical panel to start and stop the circulation and feed pumps.
- The three sulphate are added manually or mechanically (automatic belt conveyor) to the preparation vessel in presence of calculated amount of hot condensate.
- The agitation and circulation pump to be started and addition of calculated amount of ammonium nitrate of 93% concentration to adjust pH at the required value.
- After the batch is completely dissolved, it transfers to the feed tank by means of circulation pump and new batch preparation to start.
- From the feed tank, the amount of mixture is pumped to the mixing vessel in the granulation unit to start the production of multi-nutrient ammonium nitrate.

7) Operating Problems and How to resolve it?

After solving all problems faced through the addition of the nutrients, the following problems appeared and were solved:

- A) Deficiency in solubility of ferrous sulphate due to the presence of impurities, so high quality ferrous sulphate is selected in addition to installing high efficiency agitator.
- B) Phenomenon of decomposition due to decrease in the pH, and solved as mentioned before by the addition of some more ammonium nitrate solution.
- C) Blockage in the filter on suction of the granulator feed pump due problems in the solubility of ferrous sulphate in addition formation of foaming which was very viscous foams and cause also blockage of the filter and too much frequent change. This was also solved by solving the problem of solubility and problem of addition by installing and building up separate units for the preparation of the additives of nutrients and micro nutrients sources, and avoiding the direct addition to the mixing vessel.

Final Result:

Very excellent and multi-nutrient ammonium nitrate including 6 nutrients and micro nutrients in addition to nitrogen are in commercial production now without any problems.

- All parameters are under control and watching.
- Following up the product in the bulk store indicated no changes even good appearance was gained.
- No increase in temperature during storage.
- Dust free operation and product are obtained, that also very clear from the decrease in density of scrubbing solution for both granulator and cooler scrubbers.
- Dust free product means no caking tendency and that was very clear from storage.

Conclusion

- Abu Qir Fertilizers Company succeeded to have a variety of products that sustained its original products which are urea prills, urea granules, and ammonium nitrate granules by addition of secondary and micronutrients which are very important for all plants and crops.
- All problems appeared during the test were solved chemically and physically, where now all new product are in fully commercial scale without any problems.
- Abu Qir by this way opened new fields and helped the community for improving and increasing the productivity of the crops and sustained the soils by various nutrients and micronutrients to achieve nutrient balance.
- All products are registered and have its name in local market.