Fertilizers

Plants supply mankind the staple foodstuffs and other necessities of life. The plants so essential for our life require some food for their own nourishment. Plants need the following for their growth : light, water carbon, oxygen, nitrogen, potasium and phosphors. The first four are relatively aboundant in nature : water is obtained from the rains, light from the sun, carbon (in the from of CO_2) and oxygen supplied by the atomosphere. The other three, namely nitrogen, phophours and potasium although supplied by nature, are required to be furnished by artifical means.

The soils become exhausted, drained by successive crops. Each year fertiltzers have to be added to the soil to replenish (make up) the loss suffered by it on account of the growth of plants. Fertilizers are added to increase the fertility of the soil and also for the healthy growth of plants.

At least 16 elements are considered essential for the healthy growth of plants. (i) carbon, hydrogen and oxygen are obtained from air and water. These are called the natural nutrients 2) Nitrogen, phosphorus and potassium are the most vital elements. They are called the primary nutrients of fertilizer elements. 3) Calcium, magnesium and suphur are called the secondary nutrients; they are essential but needed in smaller amounts 4) Several others needed in traces are iron, manganese, boron, zinc, copper, molbdenum, cobalt and chlorine. These are called the micro-nutrients or trace elements.

Definition :

Fertilizers are compounds of certain element that are added to the soil to increase its fertility as also for the healthy growth o plants. Fertilizers are substances which are added to the soil in order to remove the decficiency of essential elements required tothe plants. The term 'fertilzer' is often restricted to artificially prepared materials containing plant nutrients.

Requisites of Good fertilizer : Every compund containing the nutrients elements cannot be used as fertilizer. The essential requisites of a good fertilizer are:

1. It must be soluble in water,
2. The fertilizer must be converted into a form that the plant can assimilate by rain or water,
3. It must be dry, finely powdered and stable (i.e., available for a long time),
4. It should not contain anything injurious to plants.
5. It should not be very acidic, and
6. It should be cheap.

Nitrogenous fertilizers :

The atmosphere is the original source of all nitrogen. In the free stable nitrogen is a very inert element. However, chemical methods have been preferred where by nitrogen can be combined with other elements into compounds which may be used in the manufacture of fertilizers. Now the possibilities for the production of synthetic nitrogen fertilizer materials are unlimited.

Effect of Nitrogen on plant growth and development :

1. Nitrogen is found in greater quantities in young growing parts of plants than in the older tissues and is especially abundant in the leaves and seeds.
2. Nitrogen is a component of protein a building block of cellular tissue.
3. It is a part of in the chlorophyll molecule, the green pigment responsible for photosynthesis.

The application of nitrogen to the soil gives dark green colour to the plants, produces rapid growth, increases protein content and yield of crops.

An abundance of nitrogen promotes rapid growth with a greater development of dark green leaves and stems. One of the most striking functions of nitrogen is the encouragement of above ground vegetative growth. However, this growth cannot take place except in the presence of adequate quantities of available phosphours, potassium and other essential elements.

An ample supply of available nitrogen during the early life of the plant may stimulate growth and result in earlier maturity. A large supply of available nitrogen encourages the production of soft, succulent (fleshy) tissue which is susceptible to mechanical injury and they attack of disease; but a normal amount of nitrogen usually increases plumpness in grains.

Deficiency Symptoms :

1. A deficiency of nitrogen is evidenced by a gradual loss of chlorophyll; this results in a light green to yellow appearance of the leaves. The entire leaf may turn yellow, even though the tissues are alive. A reduction in the chlorophyll content results in a change of colour.
2. A nitrogen-starved cucumber may have a small or pointed blossom end ; a deficiency of nitrogen may cause the kernels of cereals to become shrivelled (dry up) and light in weight.
3. In fruit trees the early shedding of leaves death of lateral buds, poor set of fruit and development of unusually coloured fruit are indications of lack of nitrogen. In brief, the deficiency of nitrogen reduces plant vifour, and the leaves become light green or yellowish green. Extreme nitrogen starvation is most likely to occur in sandy soils or water - logged soils. Fine-textrued soils with low humus content usually need additional nitrogen.

Importance of Nitrogenous fertilizers

Nitrogenous fertilizers supply nitrogen to the soil either in the form of nitrates or in the form of ammonium ion. Nitrogen is absorbed by plants as nitrate NO_3^- ion or as ammonium NH_4^+ ion. The NH_4^+ form appears to be preferred by most plants during early stages of growth and by others throughout their entire period of growth. Rice belongs to the latter category. For the most part, however absorption of nitrogen by plants is predominantly as the NO_3^- ion. This is due to the fact that the NH_4^+ ion is converted rapidly to the No_3^- ion is highly mobile and will migrate to the plant root. Thus, NO_3^- occurs normally in greater quantities than NH_4^+ and it is more accessible to plants.

Factors important in the absorption of the NO_3^- or NH_4^+ ions are as follows :

i. The uptake of the NH_4^+ ion may be limited in certain cases by an accumulation of toxic quantities of the anion accompanying it. The absorption of NH_4^+ ions favoured by a neutral or alkaline soil reaction a dilute concentration of NH_4^+ in the soil solution and a non-toxic associated anions such as HCO_3^- or CO_3^-, NH_4^+ nitrogen is absorbed more readily than NO_3^- nitrogen during the early stages of plant growth.

ii. Nitrogen in the NH_4^+ ion form appears to be preferred over NO_3^- N by those plants high in carbohydrates such as barleymaize, pumpkins and pototoes. This is becauses NH_4^+ can be utilised in protein formation after simple conversion to NH_2^- in the plant.

iii. The absorption of NO_3^- is enhanced by its mobility or ready accessibility in the soil. Its absorption is at a minimum during the early stages of growth and maximum at blossom time and thereafter.

Classification of nitrogenous fertilizers

Materials used to supply nitrogen are called nitrogen carriers and they may be classified in various ways. A convenient classification is one based on the origin or on the nature of the material. Thus, there are three general groups of nitrogenous fertilizers :

1. the non - synthetic (natural) organic materials.
2. the non-synthetic (natural) inorganic materials, and
3. the synthetic nitrogenous materials, (organic and inorganic).

a. Natural Organic Fertilizers :

The following three types are inculded in this group

i. By-products of animal origin coming from the meat and fish packing industries

ii. materials of plant origin derived from vegetable oil industries. and

iii. Other materials originating from both plants and animals. A few examples of non-synthetic organic fertilizers are given in the table.

Table - 9

Non-synthetic organic fertilizers materials

Organic Material	Total %	Water soluble N (% of total N)
Bone meal (raw)	4.2	0
Dried blood	13.8	2
Cotton seed meal	7.2	7
Horse manure	1.5	20
Chicken manure	2.3	67
Tobacco stems	1.0	47
Wheat straw	0.3	38

The mineralisation process where by N is released from organic material in a form available to plants is rather complex. In their attack on soil organic matter, the organisms involved seek out C both for energy and for growth. The use of C for energy results only in its liberation as CO_2. During growth, however, C is converted to protein and retention of a certain amount of N is necessary.

The use of organic material for soil, treatment may involve green manuring, which is the ploughing down of plants grown especially for the this purpose, or the application of animal manures or other organic substances (i.e., cotton seed cake, straw etc.,)

Natural Inorganic Fertilizers:

The non-synthetic inorganic materials may be divided into two groups: i) those obtained from natural salt deposits, such as the Chilean deposits of $NaNO_3$ and ii) those secured as a by-product; for example $(NH_4)_2\ SO_4$ obtained in the process of coal.

Chile salt petre or $NaNO_3$:

The Chilean deposits show signs of depletion and it is estimated that at the present rate of off take, the deposits, would not last for more than 250 years. At present about 75% of the world's requirements are obtained from artificial sources.

Sythetic Nitrogen Materials :

This group includes those fertilizers containing nitrogen taken from the air by any of the chemical nitrogen-fixing processes. The products fall into the following sub-divisions:

a. Organic - Examples : Urea, $CO(NH_2)_2$
Calcium Cyanamide, $Ca CN_2$.

b. Inorganic - Examples : $NH_4 NO_3$
$(NH_4)_2SO_4$ $Ca(NO_3)_2$, etc

The nitrogen content of several synthetic nitrogen materials is presented in table 10.

Table 10
Nitrogenous Fertilizers

Name of Fertilizers	Chemical Formula	Manurial ingredients (Nitorgen percent)
SYNTHETIC INORGANIC FERTILIZERS		
1. Ammonium Sulphate	$(NH_4)_2SO_4$	20.6%
2. Ammonium nitrate	NH_4NO_3	33%
3. Ammonium Sulphate Nitrate	$(NH_4)_2SO_{4+}$ $(NH_4)_2NO_3$	26%
4. Ammonium Chloride	NH_4Cl	26.2%
5. Androus ammonia Ammonia liquor	NH_3 NH_4OH	82% 24.75
6. Calcium nitrate (Nitrate of lime)	$Ca(NO_3)_2$	15.0%
7. Calcium ammonium nitrate (cal-Nitro)	$NH_4HO_3^+$ $CaCO_3$	20.5%
8. Sodium Nitrate (Nitrate of soda)	$NaNO_3$	16%
9. Nitrate of potash	KNO_3	15%N 44%K_2O
10. Ammonium phosphate (Ammo-Phos)	$NH_4H_2PO_4$ + $(NH_4)_2HPO_4$	16 N 20% P_2O_5

2. Urea, $CO(NH_2)_2$

Urea is a synthetic organic nitrogenous fertilizer. It has certain advantages over inorganic nitrates and NH_4 salts. If $(NH_4)_2SO_4$ is used then the plants absorb N from it and the SO_4^{2-} is left in the soil as a result of which it (the soil) becomes more and more acidic day by day. In the case of urea, such a disadvantage does not exist. Further, urea has fairly high N content (45%).

Upon contacting moist soil, urea is converted rapidly to $(NH_4)_2CO_3$ by a naturally occuring enzyme in soil, urease. After this change it behaves similarly to $(NH_4)_2SO_4$, although the carbonate salt causes a much more alkaline reaction than does the sulphate. The soluble carbonate resulting from the transformation of urea is capable of precipitating exchangeable Ca. The NH_4^+ ion will take place of Ca on the exchange complex. However, since the oxidation of NH_4 to HNO_3 leaves an acid residue, the Ca CO_3 that has been formed will redissolve and the soluble Ca may then re-enter exchange positions. Through this series of reactions urea is converted completely to - NO_3 and CO_2. Both will disappear from the soil without leaving a residue.

Manufacture (Commercial method of preparing Urea)

Urea has been, synthesised by the action of ammonia and carbon dioxide under high pressure and a temperature of 200°C to 210°C. Ammonium carbonate, NH_2COONH_4, is first formed and then transformed into urea.

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4$$

$$NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O$$

At ordinary pressure CO_2 and NH (react very slowly in the absence of water. If water is present $(NH_4)_2\ CO_3$ instead of ammonium carbonate, is formed. But under high pressure ammonium carbanate is formed. But under high pressure ammonium carbonate is formed. In order to keep the equilibrium shifted towards the right, an excess of ammonia is used. The reactant gases (CO_2 : NH_3 = 1:3 or 4 molecules) are passed into the reactor and a pressure of 378 atomosphere is maintained. The temperature is partially maintained by the heat of reaction at 200° to 210°C, and the rest is supplied by external heat. After several hours the equilibrium is attained with 8% conversion.

$$2NH_3 + CO_2 \rightleftharpoons NH_2COONH_4$$

Ammonium Carbanate

$$NH_2COONH_4 \rightleftharpoons NH_2CONH_2 + H_2O$$

Urea

Urea remains in aqueous solution and it is concentrated to 97% in vacuum evaporator. The 97% solution is converted into globules by spraying from the top of a tower and heated by hot air.

Phosphate Fertilizers

Phosphorus is present in all plants tissues. It is found primarily in the cell nucleus where it enters into a number of physiological reactions. Since it is so important in cell-growth processes., it is found to concentrate in the younger plant parts. During the flowering stage a relatively large proporation of phosphorus migrates into the expanding buds, and later its transfer to the seeds and fruits takes place.

Effect of Phosphorus on plant growth and development

Both plants and animals need phosphorus for proper growth. The animals derive phosphorus ultimately from plants which assimilate in directly from the soil. As a result of death and decay, plans and animals return phosphorus to the soil. But animal waste is run into the the rivers with sewage and this constitutes a serious depletion of the soil of its phosphorus. This deficiency is made up by the application of artificial phosphatic fertilizers.

The application of phosphorus to the soil stimulates early root formation and growth, and besides giving vigorous start to the plants it stimulates flowering and seed formation.

The effects of too little or too much phosphorus on plant growth are less striking than those of nitrogen or potassium. It appears to hasten maturity more than most nutrients, as an excess stimulates maturation. Phosphrous favours roots development and tillering. It tends to overcome the effect of excess of N which has been applied to P-dificient soils. Phosphorus deficiency is characterized by stunted plants having about equally affected root and top growth. Phosphorus improves the quality of feeds, especially forage for animals. Cattle fed on low-P forage gain weight very slowly and never attain maximum size.

Deficiency symptoms :

Symptoms of phosphorus deficiency in plants are not distinct. If phosphorus is deficient, cell division in plants is retarded and growth is stunded. A dark green colour associated with a purplish coloration in the seeding stage of growth is a symptom of phosphorus deficiency. Later plants become yellow. The yellowing is associated with early maturity but is definitely a symptom of phosphorus starvation. Bronze or purple leaves sometimes are observed at the top of new shoots of phosphorus, starved apple trees. In the absence of sufficient phosphorus general maturity of the crop and seed formation are usually delayed. Perhaps the most characteristic symptom of phosphorus deficiency is the stunted growth.

Kinds of phosphate fertilizers

The principal sources of phosphates, are the natural deposits of phosphorus-bearing rocks, iron ores and animal bones. The phosphatic fertilizers may be classified as follows:

1. the natura' phosphorus, such as ground rock phosphate and bone meal.
2. the treated natural phosphates, such as bone ash, bone black, super phosphates, calcined phosphates and calcium meta'phosphates;
3. the by-product phosphates, such as basic slag and
4. the chemical phosphates such as ammoniated end nitrated superphosphates, potassium phosphate, potassium metaphosphate and similar compounds.

A list of the principal phosphate fertilizers together with their approximate content of phosphoric acid is given in the table 10

Table 10
Phosphate Fertilizers

Material	Percent available P_2O_5	P	Remarks
1. Rock phosphate $Ca_3(PO_4)_2$	25–35	11–15	Effectiveness depends on degree of fineness, soil conditions, etc.
2. Super phosphate, $Ca(H_2PO_4)_2$ $CaSO_4$	16–20	7.0–8.8	Made by treating ground phosphate rock with H_2SO_4
3. Triple super phosphate Ca $(H_2PO_4)_2$	40–50	17.6–22	Made by treating ground rock phosphate with H_3PO_4
4. Basic slag	5–20	2.2–8.8	By-product obtained in the manufacture of slag.

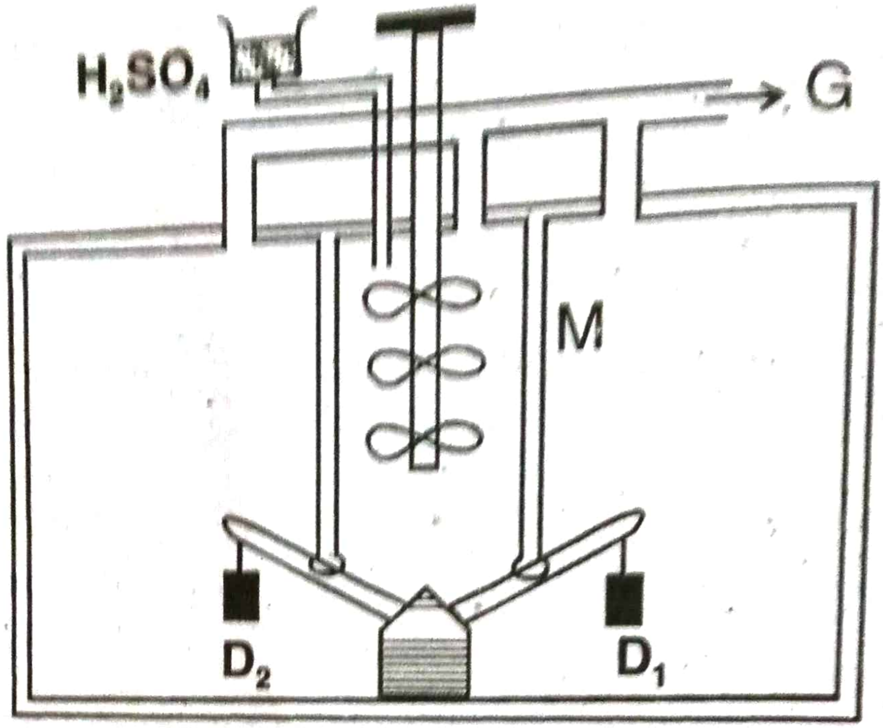

figure 13
Manufacture of Superphosphate

from the mixer are run into the same pit till it becomes full. Then it is allowed to stand for a few days. When it has become quite dry, it is dug out of the pit and meanwhile the second pit is filled.

The gases from the mixture and pits are washed with a spray of water in two successive towers. The resulting HF solution is neutralized with Na_2CO_3 to form NaF. Alternatively, it may be treated with washed sand to form hydrofluosilicic acid, H_2SiF_6, which is later neutralized with Na_2CO_3 yield respectively Na_2SiF_6 or $MgSiF_6$ which are valuable by products. The former is employed as an insecticide and the latter as pre-servative of cement surfaces.

The superphosphates are extensively used as fertilizers in agriculture. Being soluble in water, superphosphates have an advantage over normal calcium phosphate since they can be easily assimilated by the plants.

2 Bone meal

e. Triple superphosphate :

It usually contains 43 to 50% available P_2O_5. It is three times more concentrated phosphate manure than calcium superphosphate. It is an excellent fertilizer. It consists of almost pure $Ca(H_2PO_4)_2$ and it contains very little gypsum. Ground rock phosphate is mixed with requisite quantity of phosphoric acid H_3PO_4 in a mixer and agitated for several hours. The dried triple superphosphate is screened by vibrating screens, and then is made ready for sale.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow 3Ca(H_2PO_4)_2$$

f. Ammoniated superphosphate :

At present we require fertilizers which would give two essential elements to the soil. e.g., ammoniated superphosphate

$$NH_4H_2PO_4 + CaHPO_4 + Ca_3(PO_4)_2$$

Ammonium of superphosphate and triple superphosphate yields mixed fertilizers having the desirable properties of chemical stability, uniformity of texture and moisture resistance. It is produced by spraying ammoniation solution (of the composition : $NH_4\ NO_3$ = 65%,

Potassium Fertilizers

Function of potassium on plant growth :

The application of potassium imparts to the crops increased vigour, winter hardiness and sufficient strength to resist disease. It also increase lumpness of the seed and also helps in the formation of carbohydrates.

Nearly all of the potassium absorbed by plants remains in a soluble, ionic form. It is not found in cell nuclei but occurs in the cytoplasm of all plant parts. The exact function of potassium in plants is not known, but it appears to be important in

1. the formation of protein and carbohydrate.
2. the synthesis of chlorophyll
3. the transformation of NO_3^- to NH_2^-
4. the absorption of anions such as NO_3^-, $H_2PO_4^-$, and HPO_4^{2-} and
5. the storage of carbohydrates.

Because of the last function, potassium has an important bearing upon the quality of plants and plant products. The storage and cooking quanlity of potatoes is impaired if grown on K-deficient soil. Wheat and other small grains produced under low potash ferility frequently have weak systems.

Deficiency Symptoms : 2m.

A deficiency of potassium usually shows up a "leaf scorch" in most plants. Soils low in available potassium produce plants with dull green leaves. If the deficiency becomes severe, edges of the leaves turn yellow and finally die, producting a characteristic deficiency symptom known as 'tip burn'. Potato plants indicate a potassium defiency by a marginal scorch on the lower leavers, and frequently the areas of potato leaves bulge out giving a wrinkled appearance. A cucumber starved for potassium grows with a small stem end.

Classification into Chloride and Non - Chloride forms :

Potassium is obtained primarily by mining underground salt beds. Brine from salt lacks is also a source of some importance. The principal potash carriers are potassium chloride (commonly called muriate of potash) potassium sulphate (ofter referred to as sulphate of potash) potassium nitrate and manure slats. Manure salt is a semi-regine product.

Complex Fertilizers and Mixed Fertilizers

Introduction :

Soils differ greatly in their ability to supply the available nutrients to the crops. Also the mineral requirements of different crops are quite variable. In order to supply nutrient deficiencies in soils and to meet the various requirements of different crops fertilizers containing two or more essential elements are prepared. Materials which contain two or more "fertilizer elements" are mixed in proper proportions to furnish the desired amount of the nutrient elements and they are known as mixed fertilizers. For example, a 5-10-10 fertilizer means that it contains 5% nitrogen 10% phosphorus as P_2O and 10 potassium as K_2O. Some mixed fertilizers contains only two of the three primary plant-nutrient elements and are called incomplete fertilizers. The most commonly used incomplete mixtures contain phosphorus and potassium but no nitrogen. Mixed fertilizers containing all the three of the primary fertilizering elements fertilizers are called complete mixtures. Such fertilizers are also known as NPK fertilizers. For example an ammonia solution, triple superphosphate, muriate of potash and a very small amount of organic matter might be used if a complete fertilizer is desired. These fertilizers contain nitrogen as nitrates, urea or ammonium salts, phosphorus as superphosphate and potassium as chloride or sulphate.

Examples : Complex NPK, 17-17-17, 14-28-14

Manufacture

The manufacture of mixed fertilizers can be a relatively simple operation, especially if the mixture is to be of low grade (i.e., a fertilizer containing comparatively low percentage of nutrients). It consists essentially in mixing suitable materials in the correct proportion to give the desired grade.

In addition to supplying nitrogen phosphorus and potassium in desired porportions, a commercial fertilizer should have a good physical condition. It should be drillable when first purchased and should remain in this condition after storage. Mixtures of certain materials cannot be used because of their tendency to "set up" or harden. Of the fertilizer materials commonly found in mixed goods, ammonium nitrate, ammonium sulphate and potassium chloride are most likely to develop unsatisfactory physical condition. The extreme deliquescence of some of the salts especially urea and ammonium nitrate, tends to make mixed fertilizers sticky and thus reduce the drillability.

In the manufacture or superphosphate, after the acidulation of rock phosphate the product is allowed to stand for a considerable time to "cure" before being ground (powdered). This is also necessary in the preparation of ammoniated superphosphate. If these phosphates are not properly "cured", the chemical reactions involved are not completed and the fertilizer made from them will harden in the bags.

Superphosphates or other materials which have an excess of sulphuric acid, are greatly improved in their drilling qualities by the use of dolomitic lime stone as a filler because it neutralizes any excess acidity.

The drilling qualities of certain mixed fertilizers made from fertilizer salts, which take up moisture readily, can be appreciably increased by adding an organic filler such as much. A filler in what is needed to insure a good physical condition of the fertilizer.

Composition

The composition of several materials containing two or more fertilizer elements is given in table. 12

Table - 12
Some carriers containing more than one nutrient

	Fertilizer	Percentage		
		N	P	K
1.	Potassium nitrate	14	-	37.3
2.	Potassium ammonium nitrate	16	-	22.4
3.	Potassium metaphosphate	0	26.4	33.2

4.	Mono ammonium phosphate	11	26.4	-
5.	Diammonium phosphate (DAP)	11	26.1	-
6.	Ammoniacal superphosphate	5.6	7.0-7.5	-

The efficiency of a fertilizer is determinaed by the uniformity with which it can be distributed and by its quality or its chemical composition. A fertilizer is said to be of good quality if it does not cause injury to plants, does not leave any harmfull residual effect in the soil and contains the nutrient elements in proper balance. High-grade mixed fertilizers, which meet these requirements, are being made in graunlar from to insure good drillability.

Calculation of mixture fertilizer formula :

In calculating formulas for mixtures it is necessary to decide first what percentage of nitrogen, available phosphoric acid and water-soluble potash are desired in the fertilizer mixture and then water materials are to be used in making the mixture.

For example, to make 2000 kilograms of 6-12-12 fertilizer using the following ingredients :

Ammonium nitrate	33% nitrogen
Superphosphate	20% available phosphoric acid
Muriate of potash	60% water - soluble potash

The problems is to find out how much of each of these materials in needs. This may be done by use of the equation.

$$X = \frac{A \times B}{C}$$

Where X = kg of carrier required,

A = kg of mixed fertilizer required

B = percentage of N desired in the mixture

C = percentage of N in the carrier (ammonium nitrate)

Substituting the values in the above equation.

i) the ammount of ammonium nitrate required $= \frac{2000 \times 6}{33} =$

$= 364$ kg

ii) the amount of superphosphate required $= \frac{2000 \times 12}{20}$

$= 1200$ kg

iii) the amount of muriate of potash required $= \frac{2000 \times 12}{60}$

$= 400$ kg

The total amount of materials used in the fertilizer mixutre (364 + 1200 + 400 = 1964 kg). It is necessary to add 36kg of filler or physical conditioner to make 2000kg of the requried mixture

4. **Secondary nutrients :**

Of the fourteen essential elements obtained from the soil by plants, six are used in relatively large quantities and are referred to as macronutrients. They are nitrogen. Phosphorus, potassium calcium, magnesium and sulphur. Plant growth may be retarded because these elements are actually lacking in the soil, because they become available too slowly or because they are not adequately balanced by other nutrients.

Nitrogen, phosphorus and potassium are commonly supplied to the soil as farm manure and as commercial fertilizers. They are called primary (or fertilizer) elements. Calcium, magnesium and sulphur are referred to as secondary elements. Calcium and magenesium are added toa cid soils in limestone and are called lime elements. Sulphur is used in in large amounts by most plants but is usually found in considerable quantities in the soil. In areas close to industrial centres sufficient sulphur to supply crops is brought down by rain and snow from the atmosphere. Sulphur usually goes into the soil as an ingredient of such fertilizers as farm manure, superphosphate ad sulphate of ammonia, or is applied alone as flowers of sulphur, The ionic forms in which these nutrients are present in the soil and the effect of soil reaction on their availability have been already discussued under "Soil Reacion."

MICRO NUTRIENTS

The eight nutrient elements - namely, iron, manganeses, copper, zine, boron, molybdenum, chloride and cobalt are used by higher plants in very small amounts. They are called micro-nutrients or trace of elements. Such a designation does not mean that they are less essential than the micro-nutrients but merely that they are needed in small quantities.

Trace elements are found sparingly in most soil, and their availablility to plants is often very low. The cumultive efect of crop production over a period of years may repidly reduce the limited quantities of these elements originally present in the soils. The three general soil situations where micro nutrients are most apt to be a problem are :

a. sandy soil
b. organic soils and
c. very alkaline soils.

This is due to the relatively small quantities of micro-nutrients are most apt to be a problem are :

a. sandy soil.
b. organic soils and
c. very alkaline soils.

This is due to the relatively small quantities of micro-nutrients in sands and organic soils and to the low availability of these elements under very alkaline conditions.

a. Functions in plants :

The specific role of the various micro-nutrients in plan and microbial growth processes is not well understood. However these elements are known to be associated with certain essential process (Table 13).

Table 13

Functions of Micro - nutrients

Micro - nutrient	Functions in higher plant processes
Zinc	Formulation of growth hormones ; promotion of protein synthesis ; seed and grain maturation.
Iron	Chlorophyll synthesis : oxidation-reduction in respiration constituent of certain enzymes and proteins.
Copper	Catalyst for respiration, enzyme constituent chlorophyll synthesis, carbohydrate and protein metabolism.
Boron	Protein synthesis ; nitrogen and carbohydrate metabolism ; root system development ; fruit and seed formation.
Manganese	Nitrogen and inorganic acid metabolism ; carbondioxide assimilation (photosynthesis) carbo hydrate breakdown ; formation of riboflavin ascorbic acid, etc.,
Molybdenum	Symbiotic nitrogen fixation and protein synthesis.
Cl. Like Fe	Chlorophyll and protein synthesis.
Co. Like Fe	Chlorophyll and protein synthesis.

It has been suggested that several of the trace elements are effective through certain enzyme systems. For example copper. iron and molybdenum are capable of acting as electron carriers in enzyme systems which bring about oxidation-rèduction reactions in plants. Apparenty such reactions, essential to plant development and reproduction, will not take place in the absence of these micro - nutrients. Zinc and manganese also function in enzyme systems which are necessary for important reactions in plant metabolism.

Molybdenum and managanese have been found to be essential for cetain pitogen transformations in micro organisms as well as in plants. Molybdenum is considered to be essential for the process of nitrogen fixation. Also, it must be present in plants if nitrates are to be metabolized into amino acids and proteins.

Zinc is involved in the formation of some growth hormones and in the reproduction process of certain plants. Coppe is involved in respiration and in the utilization of iron. A boron deficiency decreases the rate of water absorption and iron is essential for chlorophyll formation and for the synthesis of proteins.

Chlorine and cobalt are the elements whose essentiality has been determind most recently. The role of chlorine is still somewhat obscure; however, both root and top growth seem to sugger if it is absent. Cobalt is essential for symbiotic fixation of nitrogen. This element is a component of vitamin B_{12} which is required in nitrogen - fixing nodule tissue.

b. *Materials containng micro nutrients*

Parent materials tend to influence the mircro nutrient contents of soils. Deficiencies of trace elements can be related to the low contents of the micro nutrients in the parent rocks or transported parent material. Similarly, toxic quantities are related to abnormally large amounts in the soil-forming rocks and minerals.

Inorganic forms :

Sources of the eight micro nutrients vary markedly from area to area, Because of the extremely small quantities of some of these elements present in soils and in rocks, little is known about the specific compounds in which they are found. Except for iron and manganese, which are present in many soils in large total quantities, acurate analysis for micro nutrients in soils and cools have not been made (Table 14).

Table - 14

Major natural sources of the the micro - nutrients

Element	Major forms in nature	Suggested
Iron	Oxides, sulphides and silicates	25,000
Manganese	Oxides, silicates and carbonates	2,500
Zinc	Sulphides, Oxides and silicates	100
Copper	Sulphides, hydroxy carbonates	50
Boron	Borosilicates, borates	50
Molybdenum	Sulphides, molybdates	2
Chlorine	Chlorides	50
Cobalt	Silicates	8

(ppm - parts per million)

All micro nutrients have been found in varying quantities in igneous rocks. Iron and manganese have prominet structural positions in some of the original silicate materials. Others such as cobalt and zinc may also occupy structural positions as minor replacements for the major constituents of silicate minerals including clay.

As mineral decomposition and soil formation occur, the mineral forms of the micro -nutrients are changed just as macro-nutrients are changed just as macro nutrients. Oxides and in some cases, sulphides of elements such as iron, manganese and zinc are formed. Secondary silicates, including the clay minerals, may contain considerable quantities of iron and manganese and smaller quantities of zinc and cobalt.

Organic Forms :

Organic matter is an important secondary source of some of the micro - nutrients. They seem to be held as complex combinations by the organic colloids. Copper is especially tightly held. Although the elements held are not always readily available to plants, their release through decomposition is an important fertility factor.

Manures

(Organic manures - Agricultural industrial and urban waste)

Manure is one of the most important agricultural by products. Not only does it supply organic matters and plant nutrients to the soil but it is associated with animal agriculture and with forage crops (food for cattle and horses).

Manure is a perishable product and is frequently subjected to serve losses. In the past, animals were largely dispersed on the land making possible the essay and economical application of manure to the nearby soils. But at present, thousands of beef swine and poultry are all managed in centralized locations. Further more offensive odours and runoff during wet weather have ranked animal manures so produced as one of the nation's serious air and water pollution problems.

Differences between fertilizers and manures :

Fertilizers and manures are applied to the soil in order to supply the nutrients in a readily available form to the plants.

1. Manures are the organic by products of the farm ; they are obtained from natural sources. But fertilizers are mostly inorganic compounds and they are synthetically (artifically) prepared in the factories.
2. Manures are perishable products and are subjected to severe losses. But feritilizers are fairly stable.
3. The most important inorganic fertilizers are nitrogenous, phosphatric and potassio. Examples : Urea, superphosphate and pottassium chloride. The important organic manure are farm - yard manure, compost and oil - seed cakes.

Bulky organic manures

1. Soil fertility is maintained much easily by a live stock system of farming. This is true because a large share of the nitrogen and minerals in the crops fed and of the organic matter, is excreted, by the animals. However, not all the plant - food elements of the organic matter in the feed is excreted in the manure. A portion or the nutrients and organic matter is taken by the animal in order to have for energy for performing work and have nutrients for growth and body maintenance.

Farm - Yard Manure (Fym)

It is the name given to the manure produced in the farm, chiefly with animal excreta. It is also known as stable manure, barn manure, dung and cattle manure. It is made up of the excreta of the farm animals, the litteror bedding provides for them and miscellaneous farm and house - hold wastes. The quantity of manure excreted by 1000 pounds of live weight of different farm animals is given in Table 15.

Table - 1.5

Quantity and composition of fresh manure excerted by farm animals

Animal	Excrement Feces / Urine Ratio (soil : Liquid)	H_2O%	Manure / (lb/ton) N	P_2O_5	K_2O_4
Cattle	80:23	85	10.0	2.7	7.5
Poultry	100:0	62	29.9	14.3	7.5
Sheep	67:33	66	23.0	7.0	21.7
Horse	80:20	66	14.9	4.5	13.2
Swine (pigs)	60:40	85	12.9	7.1	10.9

Complex chemicals changes occur in the food in the digestive tract of animals. These changes are brought about partly by digestive enzymes and partly by the numerous bacteria which live in the essential tract.

20% to 30% of the dry weight of the soil excrement consists of living and dead cells of bacteria.

The various consituents of feeds undergo different rates and different degrees of decomposition. Sugars and starches are easily broken down; celluloses are less easily decomposed. And lignins are very resistant. Proteins very in their case of decomposition. Approximately one - half of the organic matter in the feed is decomposed during degestion.

Most of the potassium in the feed is absorbed and excreted in the urine. Only a small fraction of the phosphorus is so absorbed ; most of the a phosphorus in manure is carrie in the solid fractions.

Composition :

Manure, as it is applied in the field is a combination of feces, urine, bedding (litter) and feed wastage which is incidentally incorporated as the animals move about thetr housing structures. The chemical composition of this material varies from place to place.

i. The moisture content of fresh manure is high, commonly varying from 60 to 85%. This excess water is a nuisance if fresh manure is spread directly on the land. Much energy must be devoted to handling and transporting the water as well as the solids.

ii. Manures are to a considerable extent partially degraded plant materials. Animals utilize only about one - half the organic matter in their feed. The bulk of the soil matter in manures is therefore, composed of organic compounds similar to those found in the feed which the animals consumed.

iii. One other important organic component of animal manures is the live component i.e., the soil organisms. Especially in the cause of cattle and sheep, the manures are teeming with bacteria and other micro - organism. Some, of organisms continue to break down constituents in the voided feces and participate in decomposition of the manure in storage.

Handling and storage practices

A generation ago, manure storage and application was a simple matter. Some farmers spread manure daily or allowed it to pile up until time and soil conditions permitted it to be spread. The coming of confined and concentrated animal management has drastically changed this situation.

The primary objective in the care and handling of form manure is to prevent loss of plant nutreints as much as possible. Even under the most favourable condition. It is practically impossible to prevent some loss of nitrogen and also some loss of organic matter. There is no difficulty in conserving the phosphorus and potassium compounds because they are not volatile.

Four general management systems are being used to handle farm manures ;

i. collection and spreading of the fresh manure daily.

ii. storage and packing in piles and allowing the manure to ferment before spreading.

iii. aerobic liquid storage and treatment of the manure prior to application

iv. anaerobic liquid storage and treatment prior to application.

a. *Applying fresh manure daily :*

The manure is scraped or otherwise moved mechanically into spreaders, sometimes reinforced with superphosphate and spread daily on the land. The obvious advantage is the prevention of loss by decompostion volatilizatson, there by maximizing the quantity of nutrients applied to the soil. One drawback is the loss of nutrients resulting when the manure is spread on frozen ground.

b. *Storage or packing in plies (fermentation) :*

Manure may be allowed to accumulate or may be removed to a pile near by. If the manure is not allowed to dry out below 40% moisture, fermentation will occur. Depending upon the moisture content and the degree of compaction, both anaerobic and aerobic break down takes place. The most abundant products of decay are carbondioxide and water along with considerable heat. Reactions involving elements such as N, P and S are of greater significance. For example, urea is hydrolyzed during the decomposition process, yielding ammonia.

$$CO(NH_2)_2 + 2H_2O \longrightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 \longrightarrow 2NH_3 + CO_2 + H_2O$$

If conditions are favourable for nitrification, nitrates will appear abundance. Either from of concentrated inorganic nitrogen can be lo and in so doing become a pollution hazard. The ammonia lost to th atmosphere may be captured by rain and snow and returned to th surface. The nitrates being soluble and to unadsorbed by the soil or th manure, are subject to leaching and to movement in run off water Fermentation may provide a more satisfactory product for land applicatio than fresh manure.

c. ***Aerobic liquid treatment :***

The manure is stored in an aerated lagoon or in an oxidation ditch. By vigorous stirring, oxygen in continuously incorporated into the system, bringing about continuous oxidation. Offensive odours are kept to a minimum, although some nitrogen is lost probably as ammonia. The primary products of decomposition are carbondioxide, water and inorganic solids. Periodically the solids can be removed along with organic residues and applied to the land. The method of treatment has many advantages the most important of which is its freedom from pungent odours. However, the costs of construction and operation are high and permits some nutrient loss. This method finds its greatest use in areas where odour control must be at a maximum.

d. ***Anaerobic liquid treatment :***

This method is similar to the aeroble treatment except that no gaseous oxygen is added to encourage aerobiosis of the liquid slurry. Consequently the nature of the reactions is quite different. The reactions are similar to those taking place in a septic tank. The principal gaseous product is methane, which make up some 60 to 80% of the total. The remainder of the gas evolved is mostly carbondioxide.

$$CO + 4H_2 \longrightarrow CH_4 + 2H_2O$$

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

This method of treatment results in considerable loss of organic carbon. However, crop response to the treated product is as good as where fresh manure is added.

Storage of Manure :

In storing manure all practical precautions should be taken to keep losses at a minimum, Handling manure not only increases the expense but also decreases the value of manure by exposing it to the air, there by increasing decomposition losses.

Good storage of manure makes provision for keeping the manure heap

i. thoroughly compact,

ii. sufficiently moist but not too wet,

iii. under cover or shelter, and

iv. undisturbed during storage.

Chemical Preservatives are added to manure to decrease nitrogen losses. Their action may be due to their prevention of biological decomposition of urea and other nitrogenous compounds or due to the conversion of volative, nitrogen compounds into nonvolatile salt. To be most effective, these preservatives must be brought into contact with the liquid manure

i. Strong acids such as phosphoric, sulphuric and hydrochloric acids are effective preservatives. These chemicals make the manure acidic, prevent urea decomposition, and change the ammonia compounds into non - volatile salts.

ii. Calcium salts of strong acids - e.g., $CaSO_4$, $CaCl_2$ and $Ca(NO_3)_2$ – are of some value as preservatives. Their effect is that of changing the ammonia into stable salt.

$$CaSO_4 + (NH_4)_2CO_3 \rightleftharpoons CaCO_3 + (NH_4)_2SO_4$$

However, if the manure becomes dry, the chemical reaction is reversed and loss of ammonia may occur, iii) Superphosphate is used ratehr extensively as a preservative of manure. Ordinary grades of superphosphate (18 to 20%) contain 40 to 50% of gypsum and they are effective in preventing loss of ammonia, especially when manure become dry.

$$Ca(H_2PO_4)_2 + 2CaSO_4 + 2(NH_4)_2CO_3 \longrightarrow Ca_3(PO_4)_2 + 2(NH_4)_2SO_4 + 2H_2O + 2CO_2$$

Tricalcium phosphate formed does not react with ammonium sulphate on drying, and thus loss of ammonia is prevented (iv) Peat has not only a high liquid absorption capacity but also a preservative action on manure.

4. Concentrated organic manures and their chemical composition :

The natural organic manures are materials derived from plants and animals. a) The plant manures are those obtained from decayed plants, cotton seed meal, wood or tobacco stem ashes. Green growing plants are burried in the soil to serve as manure. b) Animal manures include dried blood from slaughter houses the slaughter house wastes such as hoofs and horns, and pedded dry fish.

i. *Oil cakes*

Oil cakes are the richest and most concentrated of cattle foods.. They are manufactured from oil bearing seeds after they have been crushed to extract some of the oil. The oil cakes are prepared from cotton seed, linseed or groundnuts. i) Cotton seed meal is a by product of the cotton seed oil industry. After the oil has been removed from cotton seed, the cake is ground, powered and sold as a feed for fattening bullucks and dairy cows or as a fertilizers. It contains about 6 to 9% nitrogen, 2 to 3% phosphoric acid and 1.5 to 2.0% potash. Cotton seed meal is the principal protein organic fertilizer material. ii) Linseed meal is the product obtained after extracting oil. It contains 5.5% nitrogen 1.7% phosphoric acid and 1.3% potash. iii) Groundnut cake is obtained after edible oil has been extracted from the groundnuts by crushing. The oil cakes are used as cattle feed and when not suitable for that purpose, are used as good plant manures.

ii. *Blood meal*

When animals are slaughtered, the blood is led away and collected in coagulating tanks. The liquid blood is dried by raising its temperature by means of steam or hot air. During this process the liquid is agitated vigorously. It is then dried carefully and ground (About 20 to 25 gm of dried blood is obtained from every 100 gm of liquid blood). It is sold as such or mixed with other fertilizers. Dried blood contains 12 to 14% nitrogen, 0.3 to 15% of phosphoric acid and 0.5 to 0.8% potash.

iii. *Fish manure*

The use of fish as a manure dates back some centuries. It consists of either the ground, whole and largely non - edible fish or the remains of the edible fish that has been used for commercial purposes.

i. Guano is a mixture of brids exrement fish bones and other fish refuse. It also consists of carcasses of young birds, fragments of fish and sea - weeds. It contains 2 to 14% nitrogen and 12% P_2O_5.

ii. Whole guano consists of the dried ground flesh of whales and contains 8 to 10% nitrogen and 10 to 12% phosphoric acid.