CHEMICAL AND ORGANIC FERTILIZERS AND THEIR RELATION TO GRASSLAND.

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A growing plant obtains energy from the sun's rays and fertility from the soil and transforms these raw materials into wholesome food for man and beast. Without plant food we cannot have plant life. . Withdrawals of soil fertility must be replenished. Farm animal manures, plant refuse, meat works manures and chemical fertilizers constitute the principal means used to offset these losses.

Dung or farm animal manure is most beneficial to any soil. In addition to the small quantities of actual plant foods applied the mechanical condition is highly improved by the humus added.

Many specific instances of earlier efforts in history to utilize and conserve organic fertilizer materials might be given. These activities have included the conversion of fish, animal and plant refuse into fertilizing material and still more noteworthy were the efforts directed at the conservation of farm and poultry manures. In the past and even today on some farms the proportion of animals to cultivated acres is such- that' manure can be used profitably in large quantities for improving the humus content and fertility of the soil generally; However, the tremendous expansion in agricultural production has made it exceedingly difficult to continue the practice generally of conserving these manures ; more especially is this difficulty apparent in a grass farming country like New Zealand where the farm animals are not housed to any extent.

The unbalanced nature of the ordinary farm manure has, however, long been recognised and the properly balanced commercial fertilizer must be resorted to, together with an intelligent study of the soil for profitable farm operations.

As a rule the matter composing a soil is made up 'of about fifteen elements that are present in any appreciable quantities. These may be grouped as follows:- .

(a) Sodium, silicon, aluminium, manganese, chlorine.

(b) Carbon, hydrogen, oxygen.

(c) Magnesium, iron, sulphur .

(d) Nitrogen, phosphorus, potassium, calcium.

These elements are combined in the form of various chemical compounds which make up the organic and mineral matter present. Carefully conducted experiments have shown that the ten elements comprising groups (b), (c) and (d) are absolutely essential. for crop production and that plants will not grow to normal maturity in the absence of any of these elements. The three elements in group (b) are obtained by the plant from air and water. The three elements in group (c) are, generally speaking, used to a comparatively small extent by the crops, while the supply in the soil is usually large. The four elements in group (d) are used to a great extent by the crops, while the supply in the soil is usually comparatively very small, This is the fundamental reason why the elements nitrogen, phosphorus, potassium and calcium in chemical combination are added to the land for the purpose of increasing crop production and are termed the critical soil elements and are therefore the basis of our commercial fertilizers.

These artificially made fertilizers are being used in increasingly large quantities to supplement farm animal manures which are far from sufficient for intensive production methods of farming in this modern, mechanised age.

The importance of the farm animal manures to grasslands becomes apparent when we take into consideration the fact that each animal on the farm is a manure producer.

Some idea of the part played by farm animals in grassland fertilizing practice may be gained from an approximate estimation of the amount produced by our more important farm animals, the cattle beast, the horse, the sheep and the pig.

It may be taken arbitarily that a cattle beast voids 57 lbs. of solid and 21 lbs. of liquid daily, equal to about 20,000 lbs. and 7,000 lbs. annually. Now from the latest returns the head of cattle in New Zealand, including dairy cows, is estimated at 4,400,000 from which a rough idea of the enormous total amount of cattle manure deposited on our grassland may be obtained.

Including lambs there are some twenty eight and a half million sheep in New Zealand and each sheep produces roughly 2 lbs. of solid excreta a day and 1 lb. of liquid, equivalent to 730 lbs. of solid and 365 lbs. of liquid per year, so that again the enormous amount of sheep manure being produced can be roughly gauged.

We have about 275,000 horses in New Zealand and each horse, produces about 33 lbs. of solid and 12 lbs. of liquid manure so that in a year the total amount produced is considerable.

Furthermore a pig voids about 5 lbs. of solids and 3½ lbs. of liquids per day which equals some 1,800 and 1,200 lbs. per annum and as there are about 660,000 pigs in this country the total annual amount of manure from this source is important.

COMPOSITION OF FARM ANIMAL MANURES.

Following is the average composition of fertilizer constituents in fresh animal manures:-

Kind of Manure:	Nitrogen (N):	Phosphoric Acid (P_2O_5) :	Potash (K_2O):
Horse manure .	0.59%	0.34%	0.52%
Cattle manure .	0.58%	0.28%	0.53%
Sheep manure .	0.68%	0.40%	0.75%

Note: The moisture content of fresh manure averages from 60 to 80%.

The averaging fertilizing constituents of well rotted farmyard manure may be compared for instance with those of well-known artificial fertilizers as follows:-

	Nitrogen.		Phosphoric acid.		Potash.		
Dressing per acre Well-rotted farmyard manure.	In Dressing.	Equivalent to Sulphate of ammonia.	In dressing.	Equivalent to 20/21% P_2O_5 Super-phosphate.	In dressing.	Equivalent to Muriate of potash.	Lime.
Tons. 10.	Lbs. 112.	Lbs. 560.	Lbs. 58.	Lbs. 281.	Lbs. 1410	Lbs. 282.	Lbs. 157.

THE IMPORTANCE OF PHOSPHATES AND SUPERPHOSPHATES.

It is generally recognised nowadays, in all up-to-date countries of the world that it is essential to apply relatively heavy dressings of artificial fertilizers containing phosphoric acid if the fertility of the land and, in particular, grassland is to be maintained and heavy crops to be secured. New Zealand uses large quantities of phosphoric acid principally in the form of superphosphate, which contains about 20 per cent of phosphoric acid (P_2O_5). This is the principal grassland fertilizer, not only in this country but throughout the world. By-product basic slag and phosphates not subjected to chemical processing such as the raw screened phosphates from Seychelles Islands and Madagascar as well as finely ground raw phosphates from Tunisia in North Africa are or have been also used fairly extensively for direct application to grass.

Taking the two principal fertilizers used for grassland topdressing purposes in New Zealand viz, superphosphate and basic slag, it is found from available statistics that in the year 1928-29, 1,603,883 acres were topdressed with 3,845,087 cwt. of superphosphate and 619,935 acres with 1,589,053 cwt. of basic slag. This represents a dressing of approximately 50 lbs. of phosphoric acid (P_2O_5) per acre or equivalent to about 2¼cwt. of superphosphate per acre. These figures would be a little higher if the other phosphatic fertilizers such as Seychelles and Tunisian phosphates had been taken into account. More recent returns would show higher figures for superphosphate, in view of the decreased use of basic slag due to its high price and the difficulty of obtaining it.

A few details may be mentioned here regarding phosphates, the mining and preparation of, which for agriculture has developed into an industry of the first magnitude.

THE SCOPE OF THE PHOSPHATE AND SUPERPHOSPHATE INDUSTRY.

When early in 1842, John Bennet Lawes commenced to experiment with coprolites (a form of phosphate rock) as a substitute for bones in the manufacture of superphosphate, he cannot possibly have foreseen the nature and extent of the industry he was initiating.

According to A.N. Gray in "Supplement to Phosphates and Superphosphates", the world production of Superphosphate for the years 1929, 1930, 1931 were 15,474,603 tons, 15,584,662 tons and 10,986,397 tons respectively. The production of phosphate rock which is chiefly used in superphosphste manufacture for the same years was 10,489,828 tons, 11,773,412 tons and 7,623,521 tons respectively. The only available figure for basic slag (A.N. Gray - Phosphates and Superphosphates) is an estimated consumption figure of 5,330,000 tons in 1928.

Note: The figures in the above paragraph are expressed in metric tons (2204 lbs.) for calendar years.

Phosphorus is almost invariably one of the constituent elements of the primitive rocks. It is found associated with lime, oxides of iron, manganese, lead and copper etc. in varying per cent ages. New Zealand rocks and soils seem to be particularly deficient in phosphoric acid, this being no doubt responsible for the great demand for phosphates on our grasslands.

Mineral phosphate rock which has been adapted to the manufacture of superphosphate, though varying widely in analysis, usually contains between 26 and 40 per cent of phosphoric acid. In modern practice any grade of phosphate rock containing below 26 per cent of phosphoric acid is usually considered too poor for other than local use, whilst 40 per cent may be regarded as the approximate maximum phosphoric acid content of all known deposits.

New Zealand and Australia are ***particularly*** fortunate in having exceedingly high grade deposits of phosphate rock on Bauru and Ocean Island&'-some 2,000 miles away in the Pacific Ooean, **as** a source of supply for superphosphate manufacture . In purity these deposits are not far off the maximum of 40 per cent already mentioned, and their supply is estimated at between 100 and 150 million tons of utilisable phosphate rock. Their importance therefore cannot, be over-estimated - in the event of war in the Pacific Ocean, should we ever be cut off from these islands our agriculture would be severely crippled.

The Composition of Nauru and Ocean Islands Phosphate.

(On moisture free basis).

Nauru Island Phosphate.		Ocean Island Phosphate.	
x Phosphoric acid (P_2O_5)	38.98	x Phosphoric acid (P_2O_5)	40.55
Lime (as CaO)	49.09	Lime (as CaO)	53.33
Oxide of Iron and alumina	0.98	Oxide of Iron and alumina.	0.48
Organic matter and combined water	3.48	Undetermined constituents.	5.64
Undetermined	7.47		
x Equal to Tricalcium phosphate	85.11	x Equal to Tricalcium phosphate	88.60

The importations of Nauru and Ocean Islands phosphate obtained from Customs returns during the last three years ending March 31st were as follows:-
1931-32, 148,060 tons ; 1932-33, 188,388 tons;
1933-34, 14'7,230 tons.

The Composition of Superphosphate.

In the manufacture of superphosphate, roughly speaking, a ton of finely ground phosphate rock is mixed with about a ton of dilute sulphuric acid. The tri-calcium phosphate of the phosphate rock is changed to monocalcium phosphate according to the following react ion: -

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = CaH_4(PO_4)_2 + 2CaSO_4.2H_2O$$

A little dicalcium phosphate is formed during the process of curing the superphosphate.

A part of the calcium or lime of the phosphate rock combines with the sulphuric acid to form hydrated calcium sulphate or gypsum. A discussion on "Gypsum and its Fertilizing Properties" is given in the appendix to this paper. A very small proportion of tricalcium phosphate may also be found as a constituent of superphosphate as marketed.

Composition of a New Zealand 20-21 per cent (P_2O_5) Superphosphate. -

	Per Cent.	Ebs. per Ton,
Moisture (Boss at 100° C.).	10.72	240
Combined water and undetermined,	12.87	288
Silica (SiO_2) &c.	1.76	39
ø Lime (CaO).	28.38,	636
Iron and Aluminium oxides (Fe203 and Al_2O_3).	0.84.	19
* Phosphoric acid (P_2O_5).	20.72	464
ø Sulphur trioxide (SO_3).	24.71	554
ø Lime and Sulphur combined in form of gypsum ($CaSO_4 2H_2O$)	53.12%	1,189 lbs.
* Equivalent to monocalcium phosphate =	34.14 per cent.	

Large quantities of sulphur are employed in the manufacture of the sulphuric acid for treating phosphate rock. In 1930-31, 24.846 tons, in 1931-32, 25,022 tons and in 1932-33, 35,265 tons of sulphur, obtained from U.S.A. and Japan were imported for superphosphate manufacture, in New Zealand.

The following are the quantities of superphosphate manufactured locally:- 1931-32, 216,049 tons, 1932-33, 296,949 tons,

Superphosphate is the basis of a large number of commercially mixed fertilizers sold under various trade names. Included under this heading we may mention a few of the principal ones prepared in New Zealand.

<u>Basic Superphosphate</u>: This is made by mixing the usual high grade, 20% superphosphate with about 15 per cent of finely ground carbonate of lime in some cases and in others slaked lime in about the same proportion is used. Burnt lime in the ratio of approximately 7 parts to 93 parts superphosphate is also employed.

The addition of lime causes the reversion or chemical change of the water soluble phosphate of superphosphate to a water insoluble form, known as dicalcium phosphate. Although insoluble in water this phosphate is readily soluble in the official or standard 1 per cent citric acid solution, which stimulates the dissolving action of the dilute acids of the soil. It is therefore more quickly available to plant life than the tricalcium phosphate or phosphate rock which is only-partially soluble in the conventional testing solution of citric acid, and is of course insoluble in water.

The basic superphosphate on our market has a water insoluble phosphoric acid content of about 18 or 19 per cent .

Mixtures of Lime and Superphosphate.

When excess of lime is added to superphosphate, only the amount of lime required to complete reversion of the monocalcium phosphate to dicalcium phosphate undergoes change. In other words to convert the water soluble phosphoric acid of superphosphate into water insoluble or citric soluble phosphoric acid, a definite quantity of lime say 15 parts mixed with 85 parts of 20 per cent superphosphate is required to bring. about the reaction; the excess lime remaining free. Mixtures of lime and superphosphate where the lime is used in excess of what is required for reversion cannot be styled basic superphosphates but should be designated basic superphosphates plus lime. The uncombined lime under the Fertilizer Act is regarded as filler or diluent .

The mixing of lime valued at ten or fifteen shillings per ton with superphosphate worth £4 or more per ton in quantities of one third or over by weight cannot, in general, be regarded as an economic procedure. In most cases separate applications of lime and superphosphate would be cheaper. The addition of one part of carbonate of lime to two of superphosphate reduces the phosphoric acid (P_2O_5) content from 20 to about 14 per cent in mixtures containing a high percentage of lime and of course the bagging and long distance "carriage of such mixtures is uneconomic.

Nevertheless there is some point in mixing lime with superphosphate for sowing with certain seeds but the use of the raw phosphates containing free lime in mixture with superphosphate seems to be regarded as 'a more economic procedure for grassland treatment.

North African or Gafsa (Tunisian) phosphates, Seychelles and Madagascar phosphates which may contain free' carbonate of lime up to as high as 16 per cent are frequently mixed in with superphcsphates and sold for grassland topdressing purposes. In such cases allowance must be made for a certain amount of reversion of tho water soluble phosphoric acid to water insoluble or citric soluble phosphoric acid, that is to say, as found in basic superphosphate, a react ion which takes place, gradually after the mixing. In a mixture of North African phosphate and superphosphate all three phosphates viz., water soluble phosphate, dicalcium or citric soluble phosphate and insoluble tricalcium phosphate are found.

Quality Considerat ions and Nomenclature of Yuperphosphat e .

Some years ago the superphosphate on the market contained 14 to 16 or more per cent of moisture, together with an appreciable amount of free acid; in addition, the physical nature of the product was soft and inclined to clog fertilizer drills. Today the article marketed is more granular and the moisture content in some cases is lower than 8 per cent.

Under the New Zealand Fertilizer act., "Filler" or "Diluent" means any substance not containing in appreciable amounts, nitrogen, phosphoric acid or potash,. which is incorporated mechanically and not by any chemical process as a component of any fertilizer; Sand is no longer being used as a filler or diluent of superphosphate. The 16 per cent P_2O_5 sup&phosphate, diluted with 18 per cent sand during manufacture, which was on the market some years ago under the designation of 36/38 per cent superphosphate - that is to say in terms of tricalcium or insoluble phosphate, is not now registered for sale under fhe Fertilizers Act. Ground rodk phosphate of lower grado than Nauru Ocean phosphate is sometimes used to break down slightly or standardize the fertilizing strength of superphosphate during the processing. This. is quite a legal procedure. However, if Additions of phosphate rock are made after the superphosphate is manufactured the resulting product is declarable as a mechanical mixture of superphosphate and raw ground phosphate;. due allowance of. course being made for a little reversion, of the monocalcium phosphate of the superphosphate to dicalcium phosphate before sale.

The trade description "44/46 per cent water soluble superphosphate" for high grade superphosphate testing 20 per cent phosphoric acid, on our market, is apt to be confusing. For comparative purposes in assessing the value of phosphatic fertilizers, it may be stated that "Phosphoric Acid" has approximately two-and-one,-fifth times the value of tricalcium phosphate (20 - 21 per cent phosphoric acid multiplied by two-and-one-fifth = 44/46 superphosphate). Phosphoric acid is the standard term now adopted throughout the world for expressing the, amount of plant food in phosphatic fertilizers. The necessity of having a standard method of description is obvious when we consider that there are several different forms in which phosphates may occur in addition to the well known tricalcium or three lime phosphate.

The four lime phosphates are:-

(a) 4 lime phosphate $Ca_4P_2O_9$ - tetra calcic (citric soluble) phosphate, as reported to be found in Basic Slag.

(b) 3 lime phosphate $Ca_3(PO_4)_2$ - Hypothetical tricalcium phosphate (insoluble), reported to be found in rock or, raw phosphates and bone.

(c) 2 lime phosphate $Ca_2H_2(PO_4)_2$ - dicalcium phosphate (citric soluble) or reverted phosphate as found in Basic Superphosphate,

(d) 1 lime phosphate $CaH_4(PO_4)_2$ - monocalcium phosphate or water soluble phosphato as found in Superphosphate.

(c) and (d) are both known as readily available phosphates.

Actually our usual high grade superphosphate commercially known as "44/46 per cent" contains only 34 per cent of monocalcium or water soluble phosphate which is equivalent to 20/21 per cent water soluble phosphorid acid and as already pointed out, if converted to read in terms of tricalcium phosphate by simple multiplicationby the factor two-and-one-fifth, would amount to 44/46 per cent.

Having regard to the molecular weight of tri-calcium phosphate and phosphoric acid, it is found that ,a unit of "phosphoric acid" may be represented by 142, and a unit of tricalcium phosphate by 310 i.e. by an additional 168 which is the molecular weight of three units of lime united with the phosphoric acid to make the compound "tri-calcium phosphate" often conveniently called "phosphate".

The relative weights of "phosphate" and "phosphoric acid" are therefore 310, and 142 or 2.18 and 1 so that, if theoretically speaking two superphosphates were guaranteed to contain respectively 2.18 per cent of phosphate and 1 per cent phosphoric acid they would have the same plant food value. It is therefore quite plain that in the case of a phosphatic fertilizer, in which, the plant food is expressed as "phosphate" it will be necessary to divide the percentage of phosphate by 2.18 in order to compare it with a similar fertilizer in which the plant food is expressed as "phosphoric acid"; Thus a superphosphate guarnnteed 42 per cent "phosphate" has less value than one guaranteed to contain 20.6 per cent phosphoric acid.

This rather detailed explanation has been given with the idea of clarifying terms used in the' fertilizer trade, which for 'years have been the cause of a great deal of confusion amongst our farmers and traders. In Australian States and in other parts of the British Empire with the possible exception of South Australia, a superphosphate is branded and sold on the basis of its phosphorid acid content. In New Zealand the registration statement and invoice certificate of the vendor provides for the disclosure of the phosphoric acid (P_2O_5) content of superphosphates. This point is emphasized in view of the fact that the legal requirement is that the fertilizing value of phosphates shall be expressed as phosphoric acid the standard term.

Other Phosphates Employed in Grassland Practice.

Basic slag, Tunisian, Egyptian, Seychelles and Walpole Island phosphates are used in grassland topdressing in New Zealand, more especially in the higher rainfall areas of the North and South Islands.

The Basic Slags for the most part have been of the Bessemer type from Belgium, Luxemburg, France and Germany - the water insoluble phosphoric acid contents ranging in general from 16 to 21 per cent and the percentage of citric soluble phosphoric acid from about 12 to 20 per cent (75 to 95 per cent citric solubility). A few open-hearth slags from England ranging in water insoluble phosphoric acid content from 11 to 16 per cent and in citric soluble phosphoric acid from 8 to 14.5 per cent (75 - 90 per cent citric solubility) have been on the market.

The Tunisian raw rock phosphates sold under various trade names come principally from the Gafsa mines in North Africa, which are run by a French Company, and are easily the largest phosphate mines in the world. The usual grade has a phosphoric acid content ranging from about 26 to 29 per cent, insoluble in water. The Tunisian phosphates are very finely ground, in some cases over 90 per cent passing a sieve of 100 meshes to the linear inch. In citric solubility the softer North African rock phosphates including the Egyptian type are approximately 40 per cent by the standard or official test. The actual citric soluble phosphoric acid in a North African phosphate containing 26 to 29 per cent insoluble in water phosphoric acid (P_2O_5) is about 10-11 per cent or equivalent to a citric solubility figure of about 40 per cent.

Seychelles phosphates which come from certain islands such as St. Pierre and Ascension in the Seychelles Archipelago and from Barren Island and Juan de Nova Island off the Coast of Madagascar are soft, screened, phosphates which have been imported to New Zealand in fairly large quantities of late years. The high price and shortage of basic slag has created a demand for these cheap, finely divided, earthy, phosphates containing a good measure of free lime. In citric solubility they are usually a little higher than the Tunisian phosphates and quite appreciably higher than Nauru and Ocean phosphates. The average phosphoric acid content seems to range between about 24 and 28 per cent (equivalent to 52-61 per cent tricalcium phosphate). Occasionally the moisture content is rather high being as mush as 20 per cent. However, if it remains in store for a time the moisture tends to dry out with a consequent increase in phosphoric acid content. The other constituents of these soft phosphates; are organic matter 10 or 12 per cent, and free carbonate of lime 10-13 per cent.

Walpole Island phosphate, another soft earthy phosphate is shipped from a small island off the coast of New Caledonia. In quality it is lower than the Seychelles type having an insoluble in water phosphoric acid content of about 1.3 per cent.

The following is the importation of these fertilizers during the last three years.:-

	1931-32.	1932-33.	1933-34.
	Tons.	Tons.	Tons.
Basic Slags.	47,776	42;022	14,982
Tunisian raw phosphate (North African) ground in Belgium.	4,738	6,024	5,432
Egyptian raw phosphate (Ephos).	-	160	350
Seychelles, Madagascar & Walpole, Soft earthy phosphate.	30,406	26,057	28,081.

The composition of basic slag as a by-product varies considerably and depends,, so far as the phosphoric acid content in the final product is concerned, upon the amount of phosphorus in the crude iron, the process used, and the changes in methods of steel manufacture:-

Composition of Basic Bessemer Slags according to von Mayer.

Constituent	Per centage Composition.
Phosphorid acid (P_2O_5).	11.0 to 23.C
Silica (SiO_2).	3.0 to 13.0
Calcium oxide (CaO).	38.0 to 59.0
Iron oxide (Fe_2O_3).	6.0 to 25.0
Manganese dioxide (MnO_2).	1.0 to 6.0
Aluminium oxi de (Al_2O_3).	0.2 to 3.7
Magnesium oxide (MgO).	2.0 to 8.0
Sulphur (s).	0.2 to 11.4

In addition to the above constituents, slags may in some cases contain fluorine and very minor amounts of t it anium and vanadium. Digressing for a moment, it is interesting to note that cows' milk contains among other comparatively rare metals and substances, minute amounts of titanium, vanadium, aluminium, iron and magnesium.

During the last few years, as previously pointed out, a proportion of our basic slag tonnage has come from England and is of the Open-hearth type. The Open-hearth slags available as fertilizers whilst varying widely in composition are somewhat similar to the Bessemer product but have as a rule a lower phosphoric acid content and a higher proportion of certain other ingredients such as silica. The citric solubilities are sometimes lower and very much lower when fluospar is added during the course of manufacture of the steel.

Proprietary Topdressing Mixtures.

In the preparation of proprietary mixed fertilizers for grassland, generally speaking, a high proport ion of phosphate, usually in the form of superphosphate or raw phosphate, is mixed with a small proportion of blood and bone or sulphate of ammonia and usually with a little sulphate of potash or chloride of potash in the form of what is termed "30 per cent potash manure salts". Some of these goods sold as "Ammonia Topdressing", "Grass Manure" *or as* "Top dressing Mixtures" contain under 1 per cent of nitrogen and less than 2 per cent of potash (K_2O) combined with about 19 per cent of phosphoric acid derived from superphosphate or other phosphates. However, it can be readily seen that such pepperpot additions of nitrogen and potash are utterly futile. For instance 0.4 per cent of nitrogen in such a mixture when applied at the rate of 2 cwt. per acre will give an acre of grass under 1 lb. of nitrogen so it is rather a pity to expect the purchaser to pay for the mixing in of such microscopic amounts of plant food.

Nitrogenous Fertilizers in Grassland Treatment.

Blood and bone, and Bonedust and other processed organic manures are not used to any extent for grassland topdressing except in proprietary mixtures. although appreciable tonnages are produced from our freezing and boiling-down works every year. Most of the blood and bone is employed directly for cropping, market gardening or for orchard purposes. These organic materials also e-nter into the composition of the many proprietary mixtures used for the above purposes. A certain amount too is exported to far-distant countries, apparently an uneconomic procedure in view of our importations of nitrogenous and phosphatkc fertilizers. Bonedust is being diverted more and more every year into local stock food channels although some of it is exported. Dried blood is used either as stock food or for blending with bonedust etc. and what additional small quantities are available of course still find a ready market in the orchard.

The production-of the above class *of fertilizer* in the, year 1931-32, according to Factory Production Statistics was as follows:- Bonedust and Bone Manure 8,041 tons, Blood manure 3,555 tons, and Blood and Bone manure 5,627 tons making a total of 17,223 tons.

Sulphate of Ammonia: Sulphate of ammonia is manufactured on a large scale nowadays at huge, modern air-nitrogen factories in Europe and U.S.A. The sulphate of ammonia used in grassland topdressing in New Zealand, more particularly in combination with superphosphate in the form of the so called ammoniated superphosphate; comes from a huge, modern synthetic ammonia factory situated at Billingham-on-Tees in England.

The process of manufacture from ammonia (NH_3) fixed from the air by combining nitrogen and-hydrogen under pressure in the presence of a catalyst is accomplished with the aid of gypsum and carbon dioxide (CO_2) as follows:-

$$2NH_3 + CaSO_4 + CO_2 + H_2O = (NH_4)_2SO_4 + CaCO_3.$$

By-product sulphate of ammonia from gas works etc.. although still produced on a large scale Overseas is not now imported to New Zealand,

Ammoniated superphosphate is made by mixing two-thirds superphosphate with one-third sulphate of ammonia.

Imports of Sulphate of Ammonia, and Other Inorganic Nitrogenous Fertilizers.

Pear:	Total Inorganic Nitrogenous Fertilizers:	Sulphat e of Ammonia.
1932-33 .	8,707 tons.	6,840 tons.
1933-34.	3,562 "	2, 813 "

Nitrate of Soda is the other principal nitrogenous fertilizer imported but is very little used in grassland practice.

Potash Fertilizers: Potash fertilizers are used to some extent in past'ure topdressing in this country mainly in Southland, Taranaki and Auckland provinces either in direct application or in mixture with phosphates and nitrogenous fertilizers in special proprietary lines.

The following table shows the average composition of potash salts used in New Zealand:-

Constituents:	Sulphat e of pot-ash:	Muriate Chloride of pot-ash :	30 per cent potash Manure Salt:	Kainit 14 per cent :
Sulphate of potash:	90.6	-	-	-
Chloride of potash:	1.6	83.5	48.6	23.7
Sulphate of magnesia:	2.7	0.4	10.2 .	-
Chloride of magnesia:	1.0	0.3	4.2	0.1
Chloride of soda:	1.2	14.5	26.2	62.3
Sulphat e of lime :	0.4		2.2	2.5
Matter insoluble in water:	0.3	0.2	3.5	10.2
Water :	2.2	1.1	5.1	1.1
Guaranteed Min. of pure potash (K_2O):	48.6	50.4	30.0	14.0

The importations of potash fertilizers obtained from Customs Returns for the past three years have been:-

1931-32	5,188 tons.
1932-33	4,144 "
1933-34	3,831 "

In this paper, which is necessarily restricted through lack of space and time, certain chemical phases of artificial and organic manure production are briefly outlined. Limited data showing quantities, composition, basis of sale, nomenclature and usage of fertilizers designed locally or imported for New Zealand agriculture, and grassland in particular, has been set out.

It is considered. that the official publication, from time to time, of chemical analyses of all types of fertilizers on our market would be of considerable assistance to farmers, students and grassland workers. Lesser known elements of fertility additional to the officially recognised Nitrogen, Phosphoric acid and Potash, contained in large and small amounts in artificially prepared fertilizers, may yet prove to be of greater importance than hitherto thought. The blending, concentration and designing of acidic, alkaline, neutral and organic fertilizers for grassland farming, our principal industry, warrants the closest study from the chemical viewpoint.

In the appendix to this paper the importance of gypsum as a constituent of superphosphate is briefly reviewed and its value as a fertilizer is also discussed; authoritative views, old and new, being given.

APPENDIX.

THE VALUE OF GYPSUM.

In the Annual Report of the Department of Agriculture for 1909 a note was included from the Chemistry Section reminding farmers that application of gypsum (hydrated sulphate of lime, $CaSO_4,2H_2O$) to many New Zealand soils was beneficial, and that it could then be cheaply obtained from South Australia. The same convenient source of supply is still open today but little if any gypsum is applied to the soil, as such, however superphosphate, which contains 50 per cent or more of gypsum in a finely divided state, is applied to the soil in very large quantities. Natural deposits of gypsum are said to be found In New Zealand (1), occurring almost everywhere in isolated groups of small masses.

There is considerable controversy among agricultural workers as to the beneficial effect, or the contrary, of gypsum in the soil and there is undoubtedly plenty of scope for further investigation. This is particularly important in view of the large quantities, in admixture with superphosphate, that are scattered on the soil each year*, more especially on our grasslands.

* In 1932-33 for instance 296,300 tons of superphosphate containing roughly speaking 148,000 tons of gypsum were manufactured,

A number of textbooks on agricultural chemistry, old and new, and general agricultural publicat ions. were consulted to see what views were expressed on gypsum and following is a discussion of some of the opinions.

Gypsum (2) applied to a soil containing potash fixed as the insoluble silicate, reacts with the silicate, rendering the potash available for plant growth in the form of the soluble neutral sulphste. Magne s ia and ammonia are similarly made availabl- by this action of gypsum; In the case of fixed potash in soils growing leguminous crops, cabbages, rape, etc., this appears to be particularly beneficial, On the other hand an experiment started in Canada in 1929 is said to have shown that gypsum had no beneficial effect (3) but according to Sir Danial Hall this may have been due to the lack of any fixed -potash in the soil. Nitrification in soils is also favoured by gypsum. Further, Storer (2) states that no evidence is lacking that gypsum, by rendering potash, etc. soluble, as described above , transfers it from the upper to the lower layers of the soil, so that the roots of plants can everywhere find a store of it.

Gypsum also provides sulphate (5) for soils lacking in sulphur which is necessary for the production of protein in the plant (6). It also, of course, supplies the fertilizing element calcium. Collins (7) points out that application of sulphur to soils in the vicinity of large towns is unne cessary owing to the sulphuric acid content of the rain.

It has been stated that owing to'its acid properties, gypsum rectifies alkaline conditions in soil, but if applied constantly it tends to render the soil acid, and treatment with lime will then become necessary. This would appear to be debateable as gypsum is stated by some authorities to be a more or less neutral compound. Gypsum is said (8) to prevent the toxic action of ammonia on young cotton plants in Carolina. Cousins (9) also states that injury to roots after application of strong liquid manure is avoided by the simultaneous appli cat ion of gypsum.

Lyon, Fippin, and Buckman (10) state that the appli cat ion of gypsum is bonef icial on s oil containing black alkali . When such soil "is to be tile-drained, the land should first be treated with gypsum, as the substitution of alkali sulphates for carbonates causes the soil to assume a much less compact condition and thus facilitates drainage". Lyon and Buckman (11) point out, however, that "its popularity has waned in recent years, since its effectiveness on soils where it has long been used has apparently decreased, This, possibly, has been due in part to the acid residue that ultimately must result from the use of such material, and to the failure to liberate potassium - a property with which it has very generally been credited and. which, when applied to some soils, it' may possess ." It is stated to be beneficial on soils lacking in lime (12) where leguminous crops are grown and improves the permeability of wet, heavy clay, and irrigated or alkaline soils (6), (13), but in these respects it is not a substitute for lime.

A minor use of gypsum is to preserve the free ammonia in manure heaps. When sprinkled freely on the heap, it combines with the ammonia and keeps it in the heap instead of allowing escape into the air. For this reason, too, it can be used to advantage as a deodorant on the floors of stables. Superphosphate which is heavy loaded. with gypsum is used for this purpose in Canada and U.S.A. Dusted on to vines it is said to be effective against insects (14), and applied to the soil to prevent rotting of roots due to the most diverse fungi.

Thus it is evident that distinct advantages are derived from the application of gypsum to certain soils, or to soils in certain conditions. On the other hand gypsum, with an acid reaction, cannot be used to replace lime, with an alkaline reaction. Sir E.J. Russell (15) raises a doubt as to whether potassium is even dissolved out when soil is shaken with calcium sulphate solution. Johnson (16) states that "gypsum does not exert any beneficial action in consequence of directly attracting moisture," and that (17) it is only sparingly soluble in water, "and being almost universally distributed in the soil, is rarely absent from the water of wells and springs." Storer (2) considers it too slow and feeble, more an excitant than a direct form of plant food, and seldom recommended if other forms of lime are available. Murray (18) suggests that, if anything in the nature of a filler be required in fertilizers to facilitate distribution, "a suitable quantity of dry soil does equally well".

However, it has been shown above that gypsum is advantageous to soils and plants under certain conditions, and Sir E.J. Russell (19) points. out that,- "No recent experiments have been made with it, but a considerable quantity is always present in superphosphate (a ton of super contains 10 cwt. or more of gypsum): and as most farmers buy large quantities of this material, we can still include gypsum among tho substances added, although unintentionally, to the soil. It would be interesting and valuable to have tests made, because it might happen that the material had considerable value in certain special conditions."

Attention is drawn by Bear (20) to the need for a full investigation into the action of gypsum in various soils, owing to the development of the double superphosphate industry, as the concentrated superphosphates contain very little if any calcium sulphate. If rock phosphate is treated with an excess of sulphuric acid, phosphoric acid is formed, which can be separated in solution from gypsum, and this phosphoric acid may be used to treat additional phosphate rock. The resulting concentrated. superphosphate contains more than twice as much phosphoric acid (P_2O_5) as the standard form of superphosphate. Its phosphoric acid content ranges between 40 to 50 per cent, the gypsum being almost entirely eliminated. Smalley (8) points out that "The whole subject of the so-called minor plant-food elements is very complicated. Literature on the subject is voluminous, but it deals for the most part with experiments in water and sand cultures and not with field experiments. The matter is rather further complicated by the fact that the fertilizer industry has been furnishing calcium and sulphur for so many years as 'incidental fertilizer constituents, If the industry should suddenly begin to omit the calcium and the sulphur, no one could say how long it would be until calcium and sulphur deficiency symptoms would appear in the crops grown, but it is my estimate that on a great many of the lighter soils, especially in the eastern states, there is danger in leaving out the calcium and the sulphur."

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