Cyanamide in Some Fertilizer Mixtures¹

By W. S. Landis

AMERICAN CYANAMID CO., 511 FIFTH AVE., NEW YORK, N. Y.

At the meeting of the American Chemical Society in Chicago in 1920, Mr. R. H. Harger, of the United States Department of Agriculture, presented a paper entitled "The Changes Taking Place in Cyanamid when Used with Mixed Fertilizers,"² in which he described the behavior of certain experimental mixtures of fertilizer materials and Cyanamid made up in gram lots in the laboratory, and reported after a certain time interval a material decrease in the cyanamide nitrogen content and a corresponding increase in dicyanodiamide nitrogen. The author remarks that this results in a considerable waste of fertilizer nitrogen, and that methods should be evolved to prevent such waste. Fortunately, the facts as stated are not found applicable to standard brands of fertilizer in which cyanamide has been properly incorporated, some studies of which form the basis of this paper.

Observation of the rapid transformation which cyanamide undergoes in fertilizer mixtures, or even when applied alone to the soil, is not new. The decomposition and transformation have been the subject of world-wide investigation, and the principles developed are applied on an ever increasing commercial scale, there being found on the market numerous chemical products, such as ammonia, urea, dicyanodiamide and the guanidines, made from cyanamide, some of them in quantities quite comparable with those obtained from other sources. The general reactions involving these decompositions have been the subject of numerous publications and need not be repeated here.³

Returning to the Chicago paper, the author's discovery that the cyanamide nitrogen as such had completely disappeared from fertilizer mixtures in which cyanamide had been used in their formulation, was by no means a new one. In the "American Fertilizer Handbook" for 1914, the transformations taking place in cyanamide in fertilizer mixtures were referred to, this subject having been investigated years before Mr. Harger's experiments.

The surprising feature of Mr. Harger's paper, however, was his conclusion that the decomposition product of the cyanamide in the fertilizer mixture was "represented principally by, and in many cases quantitatively by the formation of dicyanodiamide."⁴ According to his experimental results, a mixture of cyanamide and moist acid phosphate containing 22 g. of cyanamide and 184 g. of acid phosphate, to which 16 g. of water were intentionally added, showed that in 8 days practically 90 per cent of the cyanamide nitrogen had been transformed into dicyanodiamide nitrogen.

Now dicyanodiamide is an article of commerce and has been so for many years. Exhaustive studies have been made on its production from cyanamide.⁵ A comprehensive review of the suggestions and methods of these investigators made in the laboratory of this company have confirmed most of

their findings. By the most efficient method of procedure, coupled with the most exacting laboratory control, we were able to transform about 85 per cent of the cyanamide nitrogen in aqueous solution into dicyanodiamide nitrogen. Since the solubility of cyanamide in water is a difficult and in many cases an inefficient process, the over-all transformation efficiency from cyanamide to dicyanodiamide has always been low. Every investigator in this field has noted the fact that in this transformation only a part of the cyanamide nitrogen goes to dicyanodiamide nitrogen and this fraction seems fairly constant, irrespective of the method of making the transformation, provided such method has good foundation in fact. In large-scale work where quantities of a ton or more are operated on and control is not quite so exact as in the laboratory, our experience has shown that less than five-sixths of the cyanamide nitrogen brought in solution can be transformed into dicyanodiamide nitrogen, and about one-sixth always goes to urea nitrogen. With less exacting control and more nearly paralleling factory conditions, this fraction going to urea nitrogen is materially greater than one-sixth and we consider it good factory practice if it does not exceed one-fourth. It is extremely interesting to find that Mr. Harger's accidental method, which involves no presolution of the cyanamide whatever, should be able to transform cyanamide into dicyanodiamide at a conversion efficiency of about 90 per cent.

EXPERIMENTAL MIXTURES OF ACID PHOSPHATE AND CYANAMIDE

However, more closely to parallel fertilizer conditions, and shortly after the reading of the Chicago paper, one of the large agricultural chemical companies mixed up a batch of commercial acid phosphate and cyanamide in one of its fertilizer factories. The mixture was of the proportion of 1900 lbs. of commercial acid phosphate and 100 lbs. of cyanamide, and the pile was carefully sampled by the agricultural company's chemist. Ten days after mixing (this elapsed time taken to represent periods similar to those reported at Chicago) this sample was tested in the laboratory with the following results: On the addition of picric acid as in the Harger procedure, precipitates were obtained without the addition of silver nitrate, indicating the presence of interfering materials. This precipitate was determined to be guanyl urea, equal to ammonia 0.21 per cent. Without extreme care in observation on the part of the analytical chemist in applying the Harger method this would have been reported as dicyanodiamide. After removal of the guanyl urea, silver nitrate was added and all the conditions of the Harger method followed out, and after adding the Harger correction factor dicyanodiamide equivalent to ammonia 0.03 per cent was obtained. A direct determination of urea showed urea equivalent to ammonia 0.66 per cent. Cyanamide equivalent to ammonia was determined as 0.06 and ammonia salts in terms of ammonia as 0.05 per cent. The above accounts for 1 per cent of ammonia out of a total of 1.2 per cent, the undetermined part being insoluble ammonia and forms which the writer could not determine analytically by accurate methods at his disposal.

This large-scale experiment, checked by two independent laboratories, seems to dispose effectually of the application of Harger's conclusions to even such an unusual kind of fertilizer mixture when prepared by actual manufacturers.

In order, however, to dispose of this matter finally, a con-

¹ Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

² Published in revised form under the title of "The Changes Taking Place in Cyanamid when Mixed with Fertilizer Materials," *THIS JOURNAL*, **12** (1920), 1111.

³ *Am. Fertilizer*, **54** (1921), 49; *Gaz. chim. ital.* (1918), II, No. 4, 358; *Trans. Am. Inst. Chem. Eng.*, **8** (1915) 267; Beilstein's "Handbuch der Organische Chemie."

⁴ In the paper as printed the conclusion as above given was modified and changed in form.

⁵ G. Grube and P. Nitsche, "The Polymerization of Cyanamide to Dicyanodiamide in Aqueous Solution," *Z. physik. Chem.*, **86**, 65 (1913); G. Grube, "Technical Methods for the Production of Dicyanodiamide from Lime Nitrogen from the Standpoint of Chemical Kinetics," *Z. angew. Chem.*, **27**, I, 368 (1914); D. R. P. 252,273; 279,133; 257,769.

siderable quantity of cyanamide was moistened and allowed to stand under such conditions as to insure about one-half of its nitrogen being converted into the dicyanodiamide form. The actual analysis of this cyanamide showed 10.8 per cent dicyanodiamide ammonia and approximately an equal quantity of cyanamide ammonia. A similar mixture with acid phosphate was made with this cyanamide which was positively known to contain dicyanodiamide, but strange to say the resulting mixture showed no test for the same upon analysis. In other words, the only conclusion is that dicyanodiamide is incapable of existence in such an acid mixture prepared according to the methods of the modern fertilizer mixing plant, all of which is quite in accord with the theory of its formation and decomposition.

MIXTURES OF CYANAMIDE WITH BASE GOODS

It has been known for a long time that amino acids react with cyanamide. In the few cases actually studied and reported in easily accessible literature,⁶ the reaction products noted are excellent plant foods. A very large amount of work along the line of cyanamide reactions with amino acids has been published in the form of theses by German students, and a comprehensive review of these is being made at the present time in order to throw more light upon this phase of the behavior of cyanamide in fertilizer mixtures.

The use of rough ammoniates in base mixtures is quite common practice in this country. The resulting base goods contain the larger part of their available nitrogen in the form of amino acids, and a study has been made of the constitution of fertilizer mixtures made up by various factories from these bases with cyanamide and other ingredients. The results of a few of these studies follow.

A mixture was prepared in the proportions of 820 lbs. of a well-known base goods and 180 lbs. of cyanamide. To insure the most complete decomposition of the cyanamide, the material was allowed to stand for 30 days after mixing and before sampling for analysis. The result of the analysis, reported on the basis of the cyanamide ammonia added being taken as 100 per cent, was as follows:

	Per cent
Cyanamide ammonia.....	2.5
Dicyanodiamide ammonia.....	3.1
Urea ammonia.....	45.7
Ammonium salts.....	4.3

No part of the remainder of the cyanamide ammonia, amounting to 44.4 per cent, together with the ammonia in the ammoniated base could be positively identified in a quantitative way by any known method at our disposal. It undoubtedly represents complex amino-cyanamide derivatives for which we have no adequate analytical methods.

Two samples of ammoniated base goods, formulated 8-3-3 and 8-2-2 from two different fertilizer plants and representing material placed on the market in the fall of 1920 in large tonnage, were examined very carefully by the various analytical methods at our disposal. These fertilizers were each formulated with 70 lbs. of cyanamide to the ton of finished fertilizer and each also contained about 1400 lbs. of ammoniated base per ton. The 8-3-3 contained 13.8 per cent moisture and the 8-2-2 contained 12.87 per cent moisture, both samples having ample water to insure reaction like that reported by Harger. The other elements were tobacco stems, rapeseed mix, ammonium sulfate, potash, and filler. The samples were investigated several months after mixing and undoubtedly the chemical status had reached equilibrium. In neither of these samples was any dicyanodiamide or guanlyl urea found, nor did they contain cyanamide. Both contained urea to the extent of 30 per cent for the 8-3-3, and 15 per cent for the 8-2-2 brand, of the equivalent of the cyanamide nitrogen added, but

more than one-half of this cyanamide nitrogen could not be accounted for by any of the analytical methods at our disposal.

In view of the fact that we were looking for dicyanodiamide in these materials and were somewhat fearful that the various methods might fail to show its presence, we added 50 mg. of pure dicyanodiamide to water extracts of 8 g. of the 8-3-3 fertilizer mixture and proceeded with a determination by the Harger method. In two experiments carried out as nearly in duplicate as possible, only 39 mg. of dicyanodiamide in one case were recovered and 14.1 mg. in the other. In a third experiment where 35 mg. of dicyanodiamide were added to the water extract from 4 g. of the fertilizer, no precipitate whatever was obtained.

In view of this peculiar behavior of the 8-3-3 fertilizer, the 8-2-2 fertilizer, which was very similar in constitution, was not tested similarly at the time. Instead, a sample was obtained of a 7-7-5 brand, formulated with 820 lbs. of ammoniated base, 300 lbs. of 16 per cent acid phosphate, and 80 lbs. of cyanamide, together with 800 lbs. of tobacco stems, meal, ammonium sulfate, and muriate of potash. The moisture content of this fertilizer, which was marketed in large quantities last winter, was 9.94 per cent. No test for dicyanodiamide was obtained by any of the various methods, and dicyanodiamide was added to the sample, which was then analyzed by the Harger method. Four aqueous extracts were prepared on four samples of 4 g. each of the fertilizer, the use of the smaller samples of the fertilizer seemingly giving more accurate check results. To one of these samples 25 mg. dicyanodiamide were added, to the second 50 mg., to the third 75 mg., and one to the fourth 100 mg. In each case practically all the dicyanodiamide added was recovered by the Harger method. Of the total of 250 mg. of dicyanodiamide added in the four lots, a total of 253.2 mg. was obtained. If we assume this extra 3.2 mg. of dicyanodiamide recovered to represent the dicyanodiamide content of 16 g. of fertilizer treated, this product would have contained a total of 0.02 per cent dicyanodiamide expressed in terms of ammonia. This was the only fertilizer mixture containing ammoniated base in which the present investigators ever succeeded in recovering quantities of dicyanodiamide comparable to that added.

Feeling that possibly the tobacco stems and meals might have had some influence on the application of the Harger method to the determination of dicyanodiamide in these mixtures, we procured some samples of standard base goods from some of the large producers. One of the samples contained 2.56 per cent of ammonia, of which 75 per cent was water-soluble, and of which about 25 per cent was yielded as ammonia on distillation with magnesia. Several 10-g. portions of this ammoniated base were extracted with water and treated by the Harger method up to the point of addition of picric acid. Four portions were prepared, each corresponding to 4 g. of ammoniated base. To the first portion 20 mg. of dicyanodiamide were added, to the second portion 40 mg., to the third portion 60 mg., and to the fourth portion 80 mg. The picric acid addition and the ice bath treatment were then carried out. The portion containing 80 mg. of dicyanodiamide began to precipitate in 15 min., and the portion containing 60 mg. at the end of 25 min. No precipitates were obtained from the other portions, even at the end of an hour. All four samples were allowed to stand over night, those to which the 20 and 40 mg. additions of dicyanodiamide showing no precipitate on this long standing. From the portion to which the 80 mg. of dicyanodiamide had been added, only 54 mg. were recovered and from the portion containing 60 mg. of dicyanodiamide only 37 mg. were recovered. These experiments confirm our theories that the amino acids of the base mixture not

⁶ Richter, 3rd American Edition, 412; *Ber.*, 43 (1910), 2882; *Gaz. chim. ital.*, 45 (1915), 56.

only react with cyanamide, as is well known, but also have the property of reacting with dicyanodiamide to a certain extent, and that it would be impossible to have dicyanodiamide in a fertilizer mixture containing base goods and cyanamide when the latter is used in the recommended proportions.

In a parallel series of experiments to which cyanamide had been added, it was found that 4 g. of ammoniated base had the property of reacting immediately with approximately 15 mg. of cyanamide. Ordinarily this reaction between cyanamide and the base goods seems extremely rapid, but it was later found that the rapidity of this reaction was affected by the quantity of ammonium salts present in the aqueous extract of the base goods. The complex nature of this reaction on cyanamide prevented our obtaining any precise information which would enable us to plot the rate of this reaction with cyanamide. Certain complex guanidines, which could not be isolated and identified specifically, seemed to be formed in the presence of the ammonium salts.

CONCLUSION

From these few experimental results with samples of commercial fertilizer and special mixtures from various plants and various agricultural chemical companies, subjected to all the available analytical methods that offer any possibilities of yielding accurate results, the present writer has been entirely unable to parallel the conclusions enunciated in the Harger paper. Wherever dicyanodiamide has been found it has been in extremely small quantity, hardly exceeding the limit of precision of the method of analysis available. Every possible endeavor has been made to check the methods, prove them for their application to the case in question, or to confirm results by the use of several methods of analysis. The widest possible ranges of fertilizer mixtures have been studied. Straight mixtures of ammoniated base and cyanamide are at the present time undergoing extensive investigation with the idea of learning more of the various forms of cyanamide decomposition products therein and applying this information to the commercial fertilizer mixtures. While this work is far from complete, we have in no case encountered dicyanodiamide in even these simple mixtures. The recovery of direct dicyanodiamide additions has yielded extremely irregular results. For this irregularity we have no adequate explanation in many cases.

Methods are lacking for the constitutional analysis of these complex nitrogen compounds. Our own laboratory has been at work on these methods for years. We have reached only to the stage where we are absolutely certain of determinations of ammonium salts, cyanamide, guanyl urea, and urea.

In the case of dicyanodiamide ammonia, we are certain of the results in the absence of amino acids and other organic materials. In the majority of such cases we can check our results by transformation of the dicyanodiamide to guanyl urea and its determination as such. In the presence of amino acids we are able to prove accuracy of results in most cases, but we have records of a few examples where we cannot prove definitely whether the methods of analysis are applicable or not. In several cases we have encountered difficulties with some of the proposed methods because decomposition takes place incident to the reagents used or conditions imposed in the carrying out of the method. This has been a source of considerable difficulty which we believe has been overlooked by many of the investigators in this field who have not familiarized themselves with the character of cyanamide decompositions.

Our conclusion to-day is that in the ordinary commercial fertilizer formulated from the everyday fertilizer materials, and using cyanamide in the quantities recommended, there need be no fear of transformation to dicyanodiamide and con-

sequent loss of the plant food value of the nitrogen contained.

The complex fertilizer mixtures of to-day, and particularly those containing cyanamide, form a most attractive field for investigation of their constitution, and should be of great interest to the student of analytical chemistry desirous of investigating one of the most complicated, yet fascinating fields of his activity. The ability to determine the various forms of nitrogen in such a fertilizer mixture is very greatly desired and chemists have been coöperating and working on these methods in several laboratories for a considerable period of time; yet the field to-day is practically untouched.

Comments on Formation of Dicyanodiamide in Fertilizers¹

By J. E. Breckenridge

AMERICAN AGRICULTURAL CHEMICAL CO., CARTERET, NEW JERSEY

In experiments made by R. N. Harger,² mixtures were made to correspond to 25, 50, 75, and 100 lbs. of cyanamide per ton of fertilizer with water added so that mixture contained 10 per cent moisture. Harger writes, "It will be noticed that while the formation of dicyanodiamide is less with smaller quantities of cyanamide used in the fertilizer, yet the change to dicyanodiamide is still very considerable with 50 pounds per ton."

In view of the fact that cyanamide had been used for some years in amounts approximating 50 lbs. to the ton, this statement disturbed the fertilizer industry, and there was some doubt as to whether or not in actual fertilizer manufacture there would be the results as indicated by the above experiments. No harmful results had been called to the writer's attention by the use of cyanamide as used in mixed fertilizers.

The author, therefore, prepared a laboratory mixture of 1900 parts acid phosphate (testing 12 per cent moisture and 16.50 per cent available phosphoric acid) and 100 parts of cyanamide (old stock). This mixture was tested at once for dicyanodiamide by the method outlined by Harger, with the following results:

	Dicyanodiamide Per cent
Fresh mixture.....	0.15
24 hours.....	0.26
9 days.....	None

Again a pile of fertilizer in the factory was sampled. This contained 40 lbs. of cyanamide to the ton, the other ingredients being the usual materials entering a fertilizer mixture, with 8 per cent phosphoric acid. The fertilizer was acid in reaction and was made up as in regular manufacture, in several hundred tons to a pile. This sample was tested for dicyanodiamide, and none was found.

The sample was sent to the Bureau of Plant Industry (Soil Fertility Investigations), Washington, D. C., and under date of September 28, 1920, the reply was "The examination of this sample of fertilizer in the Laboratory here shows it to be practically free from dicyanodiamide."

Since that proportion of cyanamide in the sample submitted was about what is used in fertilizer manufacture, the result confirmed our experience in the past; namely, that in general fertilizer manufacture no dicyanodiamide is present in fertilizers as shipped to the trade when 40 lbs. of cyanamide are used in complete goods containing 8 per cent available phosphoric acid, and that the conclusion reached by Harger is not confirmed in general fertilizer manufacture.

¹ Presented before the Division of Fertilizer Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

² THIS JOURNAL, 12 (1920), 1111.