TABLE I

Volume of Dicyano- diamide Solution Cc.	Weight of Dicyano- diamide Used Mg.	Weight of Dicyano- diamide Found Mg.
50	50.0	49.9
100	50.0	49.3
100	50.0	49.8
50	34.4	35.5
100	50.0	49.2
50	56.3	56.4
25	2.5	2.3
50	50.0	49.4
25	50.0	48.9
30	100.0	93.6

DICYANODIAMIDE AND CYANAMIDE—To a solution containing 100 mg. of cyanamide (CNNH_2) in 50 cc. there were added 41.8 mg. of pure dicyanodiamide. Two such solutions were analyzed. The analysis gave 41.9 mg. and 42.2 mg. dicyanodiamide. Similar analyses carried out with the cyanamide solution alone showed no dicyanodiamide.

DICYANODIAMIDE AND UREA—A solution, containing 50 mg. of urea and 20 mg. of dicyanodiamide in 50 cc. of water gave on analysis 19.5 mg. of dicyanodiamide. A solution of pure urea containing 4 mg. per cc. gave no precipitate at all with the reagents, and the same result was secured with a urea solution containing 100 mg. per cc.

DICYANODIAMIDE AND MIXED FERTILIZER MATERIALS—A mixture was prepared consisting of acid phosphate (12 g.), ammonium sulfate (4.2 g.), potassium sulfate (1.5 g.), and dried peat (4 g.). To this were added 50 cc. of water containing 81.2 g. of dicyanodiamide. The mixture was treated with barium nitrate, barium hydroxide, etc., and the analysis carried out as described above for mixed fertilizers. The results of duplicate analyses were 81.5 and 81.5 mg. of dicyanodiamide.

A somewhat similar analysis has already been reported in one of the experiments under the heading of "microscopic appearance of the crystals."

THE CHANGES TAKING PLACE IN CYANAMID WHEN MIXED WITH FERTILIZER MATERIALS¹

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Received July 28, 1920

In an attempt to analyze an aqueous extract of a mixed fertilizer for cyanamide by the method of Perotti,² it was found that the presence of phosphates interfered, since they, too, formed a precipitate with the silver nitrate upon making the solution alkaline with ammonium hydroxide. The difficulty was overcome by precipitating the phosphates by means of barium hydroxide and analyzing the filtrate. Although the manufacturer stated that the fertilizer contained considerable quantities of cyanamide, not even a trace was found. To test the accuracy of the method a mixed fertilizer was prepared containing a known weight of calcium cyanamide (Cyanamid) whose cyanamide content was known. The accurate results obtained upon analysis showed that the method was applicable. Some days later a second sample of this

mixture was analyzed, and to our surprise it was found that all the cyanamide had disappeared. Another fertilizer mixture was now prepared, its composition being identical with the previous one, and at intervals over a period of two weeks samples were withdrawn and analyzed for cyanamide. The loss of cyanamide was very rapid, 60 per cent having disappeared in 24 hrs., and within 10 days it had practically all vanished. This at once suggested an investigation to determine, first, the cause of this rapid disappearance of cyanamide, and, second, the products resulting from the transformation.

A search through the literature showed that while a vast amount of work has been done in reference to the changes taking place when Cyanamid alone is added to the soil or is kept in storage, and that while studies have been made in regard to the changes occurring in the soluble phosphates of mixed fertilizer containing Cyanamid, it is a curious fact that no one seems to have paid any attention to the changes which may occur in cyanamide when this extremely reactive substance is mixed with other fertilizer materials. The present paper reports some results of such an investigation.

FACTORS CAUSING TRANSFORMATION OF CYANAMIDE

The fertilizer mixture which was prepared was composed of acid phosphate, ammonium sulfate, potassium sulfate, and Cyanamid (all being the usual commercial products), and dried peat. In order to ascertain which of these materials was instrumental in bringing about the rapid disappearance of cyanamide, mixtures containing Cyanamid and various combinations of these substances were prepared. Since it seemed probable that the acid phosphate was involved in the reaction it was used in each of the mixtures. The mixtures were: (1) acid phosphate and Cyanamid; (2) potassium sulfate, acid phosphate, and Cyanamid; (3) ammonium sulfate, acid phosphate, and Cyanamid; and (4) dried peat, acid phosphate, and Cyanamid. Samples from these mixtures were analyzed at intervals. While all of the mixtures caused a slight decrease in cyanamide, only Mixture 4 showed any considerable decrease, the rate here being rapid and practically parallel to that of the original mixture. This suggested that perhaps the dried peat was not so dry as the name would indicate, and an analysis of this material showed that it did contain 36 per cent of moisture. The other materials were practically dry, although the acid phosphate contained a little moisture. In a mixture containing acid phosphate, Cyanamid, and 8 per cent of water, the cyanamide decreased very rapidly, only 5 per cent of it remaining at the end of 3 days. Several similar mixtures exhibited this same rapid decrease in cyanamide content. To test the effect of moisture alone, moist quartz containing 10 per cent of water was mixed with Cyanamid. Here, too, there was a decrease in cyanamide, resulting finally in its disappearance, but the rate was by no means so rapid as when moist acid phosphate was employed, the loss of cyanamide in the latter mixture during the first day being eight times as great as that in the moist quartz mixture. On the other hand,

¹ Presented at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

² *Rend. soc. chim. ital.*, 1904, 192.

Cyanamid when mixed with practically dry acid phosphate remained unchanged even after 2 or 3 mo. This rapid disappearance of cyanamide must therefore be caused by the presence of acid phosphate and a small amount of moisture. This conclusion was further confirmed by experiments with complete mixed fertilizer, since only those samples in which these conditions existed (*i. e.*, acid phosphate and 5 to 10 per cent of moisture) showed any considerable decrease in cyanamide.

CHEMICAL CHANGES INVOLVED

Upon complete evaporation of a sample from one of the mixed fertilizers, the cyanamide of which had entirely disappeared, there was left a quantity of long needles, which were identified as dicyanodiamide by the method described in the preceding paper. A quantitative determination of dicyanodiamide, made upon another sample of this fertilizer, showed that 90 per cent of the cyanamide originally present had been transformed into dicyanodiamide. The mixture had now stood 30 days. At the end of 100 days it was again analyzed, and the results showed that the dicyanodiamide content was practically unchanged. Another mixture of Cyanamid and acid phosphate, containing about 10 per cent of moisture, was next prepared, and the changes taking place in cyanamide and dicyanodiamide content were followed by making simultaneous analyses for these two substances at intervals. Since the chemical change occurring in the formation of dicyanodiamide from cyanamide is simply the union of two molecules of cyanamide to form a molecule of dicyanodiamide, according to the equation

there is no alteration in weight, and if this reaction is the only one involved the weight of dicyanodiamide produced should equal that of the cyanamide lost; or, stated differently, the combined weights of cyanamide and dicyanodiamide should remain constant. This study served to confirm what was apparent from the results already secured: namely, that in the disappearance of cyanamide the principal chemical change was the formation of dicyanodiamide, and that under the conditions employed this was at all times practically quantitative. A similar study conducted with two complete mixed fertilizers yielded practically the same results, although toward the end of the period the amount of dicyanodiamide in the mixture did not so closely approximate the quantity of cyanamide which had disappeared, the final yield of dicyanodiamide representing only about 65 per cent of the loss in cyanamide. Whether this result was due to a parallel reaction which produced some other compound from the cyanamide—possibly urea—or whether part of the dicyanodiamide formed was subsequently decomposed into other compounds, has not yet been determined.

When Cyanamid and moist acid phosphate (6 to 10 per cent H_2O) were mixed, with or without other

fertilizer materials, a rise in temperature of 20° to 30° C. was always observed, and the mixture set to a hard mass upon standing. When analyzed immediately there was no loss of cyanamide. The acid phosphate possessed but slight acidity, 10 g. of this material requiring 27.5 cc. of 0.1 *N* alkali to titrate to the neutral point with methyl red; yet when 1 g. of Cyanamid, which required 169 cc. of 0.1 *N* sulfuric acid to reach the same end-point, was added to 10 g. of moist acid phosphate, the resulting mixture, when added to water, was always acid to litmus. An alkaline mixture could be obtained only by adding a considerably larger quantity of Cyanamid. This can only mean an interaction between the acid phosphate and Cyanamid. de Nolinari and Ligot¹ and later Brackett² showed that when Cyanamid and acid phosphate were mixed there resulted a "reversion" of the phosphate, *i. e.*, the introduction of more calcium into the acid phosphate molecule to form insoluble phosphates. When these facts are considered together, they indicate the probable course of the reaction which results in the rapid loss of cyanamide. The calcium cyanamide and acid phosphate first react to form dicalcium or tricalcium phosphate and free cyanamide:

and the free cyanamide thus produced is rapidly transformed into dicyanodiamide and other products.

Up to this point in the investigation, the fertilizer mixtures contained less than 1 part of Cyanamid to 10 parts of acid phosphate. In a mixture of moist acid phosphate and Cyanamid, containing 25 per cent of Cyanamid, there was also a rapid conversion to dicyanodiamide (practically quantitative), but only about 60 per cent of the cyanamide was thus transformed, and after this point was reached very little further change resulted. It is evident, therefore, that there is a limit to the quantity of cyanamide which a given quantity of moist acid phosphate will transform.

Reference has already been made to the fact that the mixing of Cyanamid with moist quartz caused a disappearance of cyanamide. It was found that most of the cyanamide was changed into dicyanodiamide. That this change would take place was somewhat to be expected, since Perotti³ and Hager and Kern⁴ have shown that when Cyanamid containing moisture was stored for several months a large portion of the cyanamide was converted into dicyanodiamide.

Finally, analyses were made of six samples of mixed fertilizer, containing varying amounts of Cyanamid, which had been prepared for certain 1920 field tests carried out by the Division.⁵ Four weeks had elapsed since the fertilizers had been mixed. Each sample was found to contain a large quantity of dicyanodiamide, the

¹ *J. soc. agr. Brabant et Hainaut*, **54** (1909), 161.

² *THIS JOURNAL*, **5** (1913), 933.

³ *Atti acad. Lincei*, [5] **15** (1906), I, 48.

⁴ *Z. angew. Chem.*, **29** (1916), 221.

⁵ Prepared for field tests in experimental work being conducted by Dr. O. Schreiner, Dr. J. J. Skinner, and Mr. B. E. Brown, of Soil Fertility Investigations. The mixtures were prepared according to the usual fertilizer practice, no modifications being introduced, with a view of studying any changes in the cyanamide content.

amounts of this compound ranging from 11.4 to 33.4 lbs. per ton of the fertilizer mixtures.

EXPERIMENTAL DETAILS

MATERIALS EMPLOYED. *Acid Phosphate*—This was the usual type of fertilizer material, containing 16 per cent of available P_2O_5 .

Ammonium Sulfate—The crude material of commerce, containing 25 per cent of NH_3 .

Potassium Sulfate—The salt commonly used in fertilizer, containing 50 per cent of K_2O .

Cyanamid—This was technical calcium cyanamide, a hydrated material which was about a year old and contained 21 per cent of cyanamide and 2.3 per cent of dicyanodiamide. In two of the experiments, there was used a more recently purchased hydrated Cyanamid which contained 29.4 per cent of cyanamide and no dicyanodiamide.

METHODS OF ANALYSIS—A 20 g. sample (in mixtures containing more than 6 per cent of Cyanamid, a 10 g. sample was used) of the fertilizer mixture was stirred with 50 cc. of water. To this were added 100 cc. of a saturated solution of barium nitrate and then a solution of barium hydroxide until the mixture was slightly alkaline to litmus. The barium hydroxide was added to precipitate phosphates, but when ammonium sulfate was present this would have produced large amounts of ammonium hydroxide, which would convert some of the cyanamide to dicyanodiamide. The barium nitrate was therefore added to prevent this ammonia formation. The mixture was agitated vigorously for 30 min. with a mechanical stirrer, then transferred to a 500 cc. graduated flask, made up to the mark, thoroughly mixed, and filtered. Two 200 cc. portions were measured out, and one was analyzed for cyanamide and the other for dicyanodiamide. To determine cyanamide the method of Perotti, as modified by Brioux,¹ was employed, the precipitate of silver cyanamide being dissolved in dilute nitric acid and titrated against 0.1 N ammonium thiocyanate solution. For the determination of dicyanodiamide the method described in the preceding paper was used.

CHANGES IN CYANAMIDE CONTENT OF A MIXED FERTILIZER

Fertilizer Mixture A contained:

	Grams
Acid phosphate.....	100
Potassium sulfate.....	12
Ammonium sulfate.....	42
Cyanamid.....	10
Dried peat.....	36
TOTAL.....	200

The materials were ground together in a mortar until they would pass through a 20-mesh sieve, and further mixed on a large piece of glazed paper. The mixture was analyzed immediately for cyanamide, and

TABLE I—CHANGES IN CYANAMIDE CONTENT OF A COMPLETE MIXED FERTILIZER (MIXTURE A)

TIME Days	Mg. Cyanamide per G. Cyanamid Used
Immediately after mixing	220.0
1	95.5
3	73.6
4	46.2
6	41.1
13	23.1

¹ Ann. chim. anal., 15 (1910), 341.

FIG. 1—CHANGES IN CYANAMIDE CONTENT OF A COMPLETE MIXED FERTILIZER CONTAINING "CYANAMID"

the analysis was repeated at intervals for 13 days, with the results given in Table I and shown graphically in Fig. 1.

INFLUENCE OF VARIOUS FERTILIZER INGREDIENTS

Four mixtures were prepared containing various combinations of Cyanamid with the other materials used in the previous experiments, as follows:

(a)	Grams	(b)	Grams
Acid phosphate.....	90	Acid phosphate.....	45
Cyanamid.....	10	Ammonium sulfate....	18
		Cyanamid.....	5.5
(c)	Grams	(d)	Grams
Acid phosphate.....	45	Acid phosphate.....	45
Potassium sulfate.....	6	Dried peat.....	18
Cyanamid.....	5	Cyanamid.....	5.5

The results of analyses are given in Table II.

TABLE II—CHANGES IN CYANAMIDE CONTENT OF VARIOUS MIXTURES OF "CYANAMID" AND ACID PHOSPHATE WITH OTHER FERTILIZER MATERIALS

TIME Days	(a)	(b)	(c)	(d)
Immediately after mixing	202	196	210	201
1	180	152	192	...
2	164	...	...	94
4	...	...	...	82
5	...	139	...	...
9	120	...	190	...

EFFECT OF MOISTURE CONTENT OF FERTILIZER MATERIALS

Moisture in the materials was determined by drying for 20 hrs. at 100° C.

	H ₂ O Per cent
Ammonium sulfate.....	0.4
Potassium sulfate.....	0.18
Dried peat.....	36.0
Acid phosphate.....	2.7

In the experiments described above the acid phosphate probably contained slightly more than 2.7 per cent of moisture since some weeks elapsed before the moisture content was determined, and during this time it had been stored in a paper bag exposed to the drying action of the air. At the time the experiments were performed the acid phosphate had already been considerably air-dried, so it contained much less

moisture than fresh acid phosphate, the moisture content of the latter being 6 to 10 per cent.

I—CHANGES IN CYANAMIDE CONTENT

CYANAMID AND MOIST ACID PHOSPHATE—Mixture B was prepared containing:

Acid phosphate (2.7 per cent H ₂ O), grams.....	82
Cyanamid, grams.....	10
Water, grams.....	8
Total moisture, per cent.....	10.2

The water was added to the acid phosphate and the material ground in the mortar until uniform, the resulting mixture appearing quite moist. The Cyanamid was now added and this mixture again made uniform by grinding. Almost at once all evidence of moisture disappeared, and a fine, dry powder resulted. During this change, the temperature rose from 24° to 45° C. When the resulting mixture was added to water it showed a strongly acid reaction toward litmus. The mixture was analyzed for cyanamide immediately and at intervals over a period of 6 days, the results being given in Table III.

TABLE III—CHANGES IN CYANAMIDE CONTENT OF A MIXTURE OF "CYANAMID" AND MOIST ACID PHOSPHATE (MIXTURE B)

TIME	Mg. of Cyanamide per G. of Cyanamid Used
0 hrs.	210
5 hrs.	97.6
2 days	21.4
6 days	17.3

CYANAMID AND AIR-DRY ACID PHOSPHATE—Mixture C contained:

Acid phosphate (2.7 per cent H ₂ O), grams.....	90
Cyanamid, grams.....	10
Total moisture, per cent.....	2.2

and was mixed as in the preceding experiment. Immediately after mixing it contained 223 mg. of cyanamide per gram of Cyanamid, and after standing 18 days it was found to contain 194 mg. per gram of Cyanamid used.

CYANAMID AND MOIST QUARTZ—A mixture, D, containing

Quartz (ground to 200 mesh), grams.....	90
Water, grams.....	10
Cyanamid, grams.....	11.1
Total moisture, per cent.....	9

was prepared and analyzed as in the previous experiments. There was no rise in temperature when the mixture was prepared, and it remained moist, clinging together like moist sand when the jar containing it was rotated. After a day an odor of ammonia was given off. At the end of 2 wks. it was somewhat more dry, but the particles still clung together, and it was by no means the dry powder described in the experiment with moist acid phosphate. Table IV gives the results of analyses of this material.

TABLE IV—CHANGES IN CYANAMIDE CONTENT OF A MIXTURE OF "CYANAMID" AND MOIST QUARTZ (MIXTURE D)

TIME	Mg. of Cyanamide per G. of Cyanamid Used
0 hrs.	213.6
24 hrs.	185.8
2 days	131.25
9 days	31.5

The results for Mixtures B, C, and D are shown graphically in Fig. 2.

AVAILABLE ACID IN ACID PHOSPHATE—One gram of acid phosphate was extracted for 0.5 hr. with 500 cc.

of water. The filtrate was strongly acid to litmus. Upon titration against 0.1 *N* sodium hydroxide, using methyl red as an indicator, 2.75 cc. of the alkali were required.

FIG. 2—CHANGES IN CYANAMIDE CONTENT OF "CYANAMID" WHEN MIXED WITH AIR-DRY ACID PHOSPHATE, MOIST ACID PHOSPHATE, AND MOIST QUARTZ

AVAILABLE ALKALI IN CYANAMID—One gram of the Cyanamid was stirred vigorously with 500 cc. of water for 30 min., and filtered. The filtrate, which was strongly alkaline to litmus, required 169 cc. of 0.1 *N* sulfuric acid for neutralization with methyl red as indicator.

DICYANODIAMIDE CONTENT OF THE MIXTURES—Twenty grams of Mixture B were stirred for 30 min. with 200 cc. of absolute acetone, and filtered. The acetone extract was evaporated to dryness, leaving a quantity of long needles mixed with some dark material. Recrystallization of the residue from water gave colorless needles, melting at 205°, whose melting point was unchanged when mixed with dicyanodiamide. A solution of these crystals gave yellow crystals of silver picrate monocyanoguanidine (m. p. 230°) upon treatment with picric acid and silver nitrate (Fig. 1, preceding paper). A quantitative determination of dicyanodiamide in Mixture B gave 179 mg. of dicyanodiamide per gram of Cyanamid, at the end of 4 wks. At the end of 15 wks., the mixture contained 193.5 mg. of dicyanodiamide per gram of Cyanamid used. Mixture C contained but 7.9 mg. of dicyanodiamide per gram of Cyanamid. Mixture D at the end of 9 days contained 171.2 mg. of dicyanodiamide per gram of Cyanamid used. A quantitative conversion of the cyanamide to dicyanodiamide would have required the appearance of 230 mg. of dicyanodiamide per gram of Cyanamid used.

II—SIMULTANEOUS CHANGES IN CYANAMIDE AND DICYANODIAMIDE CONTENT

CYANAMID AND MOIST ACID PHOSPHATE—The following Mixture E was prepared:

Acid phosphate (2.7 per cent H ₂ O), grams.....	184
Water, grams.....	16
Cyanamid, grams.....	22.2
Total moisture per cent.....	10.2

Analyses for cyanamide and dicyanodiamide were made immediately, and at intervals over a period of 8 days. The results are shown in Table V and Fig. 3.

TABLE V—SIMULTANEOUS CHANGES IN CYANAMIDE AND DICYANODIAMIDE IN A MIXTURE OF "CYANAMID" AND MOIST ACID PHOSPHATE (MIXTURE E)

TIME	Cyanamide (Mg. per G. of Cyanamid Used)	Dicyanodiamide (Mg. per G. of Cyanamid Used)
0 hrs.	208.9	13.5
5 hrs.	130.0	113.2
28 hrs.	75.6	175.8
2 days	49.8	184.6
5 days	44.6	180.2
8 days	30.5	182.4

The above experiment was twice repeated with practically identical results.

FIG. 3—SIMULTANEOUS DISAPPEARANCE OF CYANAMIDE AND FORMATION OF DICYANODIAMIDE IN A MIXTURE OF "CYANAMID" AND ACID PHOSPHATE

MOIST ACID PHOSPHATE AND EXCESS OF CYANAMID—Mixture F was prepared and studied in the usual way. The Cyanamid used was the more recently purchased sample containing 29.4 per cent of cyanamide. This mixture, when added to water, was alkaline to litmus.

Acid phosphate (2.7 per cent H ₂ O), grams.....	67
Water, grams.....	8
Cyanamid, grams.....	25
Total moisture, per cent.....	9.8

Table VI gives the results.

TABLE VI—SIMULTANEOUS CHANGES IN CYANAMIDE AND DICYANODIAMIDE IN A MIXTURE OF MOIST ACID PHOSPHATE AND AN EXCESS OF "CYANAMID" (MIXTURE F)

TIME	Cyanamide (Mg. per G. of Cyanamid Used)	Dicyanodiamide (Mg. per G. of Cyanamid Used)
0 hrs.	277	0
2 days	191	97
8 days	155	122
41 days	127	142

CYANAMID IN COMPLETE FERTILIZER MIXTURES—Three complete fertilizer mixtures were prepared, their composition being:

	(Mixtures G and H)	(Mixture I)
Acid phosphate (2.7 per cent H ₂ O), grams...	200	200
Potassium sulfate, grams.....	24	24
Ammonium sulfate, grams.....	84	84
Dried peat (9 per cent H ₂ O), grams.....	42	72
Water, grams.....	30	..
Cyanamid, grams.....	20	20
Total moisture, per cent.....	9.8	3.2

Mixtures G and I were prepared by grinding in the mortar. Since in actual fertilizer practice the materials are merely mixed with a shovel, Mixture H was mixed by means of a spatula. The results are given in Table VII.

TABLE VII—SIMULTANEOUS CHANGES IN CYANAMIDE AND DICYANODIAMIDE CONTENT OF THREE COMPLETE MIXED FERTILIZERS

TIME	Cyanamide (Mg. per G. of Cyanamid Used)			Dicyanodiamide (Mg. per G. of Cyanamid Used)		
	G	H	I	G	H	I
0 hrs.	223	221	210	14	10	..
1 day	143	128	..	86	100	..
3 days	102	67	201	111	126	..
15 days	..	..	199	..	..	..
18 days	14	9	..	104	136	..
34 days	..	5	201	98	136	..

DICYANODIAMIDE CONTENT OF MIXED FERTILIZERS—Six mixed fertilizers which had been prepared for use in the field tests of this Department were analyzed for cyanamide and dicyanodiamide. The compositions of the mixtures were as follows:

INGREDIENTS	Mixture, Weight in Pounds					
	(1)	(2)	(3)	(4)	(5)	(6)
Sodium nitrate.....	4.5	4.5	6.8	2.3	..	..
Ammonium sulfate....	3.4	..	..	..	..	4
Dried blood.....	..	5.3	8.4	2.7	10.7	..
Acid phosphate.....	42.7	42.7	42.7	42.7	42.7	25
Potassium sulfate....	13.6	13.6	13.6	13.6	13.6	4
Cyanamid.....	7.8	7.8	3.9	7.8	7.8	8
Sand (air-dry).....	25.7	25.8	22.3	22.9	22.9	9
TOTAL.....	97.7	99.7	97.7	97.6	97.7	50

The Cyanamid used in the first five mixtures was 2 yrs. old and contained 15.4 per cent of cyanamide and 6.2 per cent of dicyanodiamide. For Mixture 6 there was used the more recently purchased Cyanamid containing 29.4 per cent of cyanamide. The results are given in Table VIII.

TABLE VIII—CYANAMIDE AND DICYANODIAMIDE CONTENT OF 20 GRAMS OF COMPLETE FERTILIZER MIXTURES WHEN MIXED AND FIVE WEEKS AFTERWARD

MIXTURE	Cyanamide		Dicyanodiamide	
	Added Mg.	Found after 5 Wks. Mg.	Added Mg.	Found after 5 Wks. Mg.
1.....	240	89	99	214
2.....	240	106	99	211
3.....	120	40	50	114
4.....	320	171	132	249
5.....	240	142	99	201
6.....	940	648	..	334

EFFECT OF USING SMALLER PROPORTIONS OF CYANAMID—Four mixtures of moist acid phosphate and Cyanamid were prepared, containing in each 1000 g. of mixture 25, 50, 75, and 100 g., respectively, of Cyanamid. Since mixed fertilizers commonly contain about 50 per cent of acid phosphate, these mixtures would correspond to 25, 50, 75, and 100 lbs. of Cyanamid per ton of mixed fertilizer. They were prepared as in the previous experiments, using another supply of acid phosphate containing 3 per cent of moisture, to which was added water so that all mixtures contained practically 10 per cent of moisture, to approximate the moisture condition of commercial acid phosphate. In the three lower concentrations of Cyanamid duplicate mixtures were prepared, using for comparison the acid phosphate employed in the previous experiments.

After 3 days the mixtures were analyzed for cyanamide and dicyanodiamide, with the results given in Table IX.

TABLE IX—CHANGES TAKING PLACE IN 20 GRAMS OF MIXTURES OF MOIST ACID PHOSPHATE WITH VARYING AMOUNTS OF "CYANAMID"

Parts Cyanamid in 1000 Parts Mixture	When Mixed Cyanamide Mg.	After 3 Days	
		Cyan- amide Mg.	Dicyano- diamide Mg.
25	145	99	6
25	145	29	7
50	290	97	91
50	290	85	74
50	290	66	125
75	435	61	348
75	435	44	353
100	580	32	498

It will be noticed that while the formation of dicyanodiamide is less with the smaller quantities of Cyanamid used in the fertilizer, yet the change to dicyanodiamide is still very considerable with 50 lbs. per ton.

CONCLUSIONS

Further investigations are being conducted, but the results already secured seem to warrant the following conclusions, at least in so far as the conditions of concentration, temperature, and moisture here reported on are concerned:

1—When Cyanamid is mixed with fertilizer materials containing acid phosphate and 5 to 10 per cent of moisture, the cyanamide content decreases with great rapidity.

2—This change is represented partially by, and in the higher concentrations principally by, the formation of dicyanodiamide.

3—A given quantity of moist acid phosphate is able to transform a limited amount of calcium cyanamide.

4—Cyanamid is not affected by dry acid phosphate.

5—Moisture alone is able to cause the conversion of cyanamide to dicyanodiamide, but the change is much slower than when acid phosphate is present.

Since it has been repeatedly shown that dicyanodiamide is valueless as a fertilizer material, and, moreover, is toxic to many plants,¹ the formation of this compound in fertilizer materials seems undesirable. On first thought, it would appear that this conversion of cyanamide into dicyanodiamide could be avoided by employing dry fertilizer mixtures, but this overlooks the fact that when such mixtures are added to the soil, moisture conditions are at once provided, and the transformation may possibly then take place. Preliminary experiments carried out in this laboratory indicate that, under certain conditions at least, this is the case.

It should be noted that these unfortunate reactions between acid phosphate and Cyanamid do not in any sense imply that Cyanamid cannot be successfully used when mixed with other forms of phosphate. In this connection it should be noted that the Fixed Nitrogen Research Laboratory of the Ordnance Department has called our attention to the fact that lime nitrogen (Cyanamid) can be mixed with calcined and basic phosphates without the excessive production of dicyanodiamide noted when moist acid phosphate is used.

STUDIES ON THE CORROSIVE ACTION OF CHLORINE-TREATED WATER. I.—THE EFFECTS OF STEEL ON THE EQUILIBRIUM: $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO}$, AND OF PRODUCTS OF THE EQUILIBRIUM ON STEEL

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Received July 17, 1920

In the entire range of the subject matter of chemistry there is scarcely a phase upon which more work has

been done, and concerning which there is greater deviation of opinion expressed in the literature, than upon solutions of chlorine gas in water. The importance of a thorough knowledge of such solutions lies in the fact that so many distinct fields are concerned. The physical chemist is interested in all phases of the equilibrium established between the products of the reaction

and how this may affect the properties of each substance. The bacteriologist and sanitary engineer are concerned with the amount of chlorine it is necessary to add to natural waters in order to render them potable. The physiologist is interested in discovering the effect upon bodily functions and metabolism of the introduction of chlorine-treated water into the alimentary canal. The fields of the engineer and metallurgist converge in considering the effect of chlorine water upon the corrosion of iron and steel pipes and upon steam boilers.

Applications of this problem have been widely recognized, as is indicated by the numerous papers to be found touching in varying fashion upon some phase of the subject. There are two outstanding facts to be gained from a survey of the literature: first, the extremely qualitative nature of the great majority of these reported observations; and hence, second, the wide differences of opinion, even to the point of diametrical opposition, on some of the most fundamental points of the chemistry, corrosive effects, and physiological action. It is not within the scope of this paper to undertake any extensive critique of the work which has been done; the work which may be considered most authoritative will be referred to later. With these large discrepancies and rather serious omissions in the present knowledge of the solution of chlorine in water clearly in mind, this series of researches has been undertaken with the ostensible purpose of attempting to bring order out of an indefinite and unsatisfactory state of a scientific subject, with especial reference to the application to the city water supply of Nashville, Tennessee.

Of course, of the greatest importance from any standpoint is the question whether or not city water which has been treated with chlorine is physiologically injurious when used for drinking purposes. There is not to be found in the literature a record of any complete biological research of this kind, though work upon the effect of chlorine gas in respiratory processes is extensive and conclusive since the war. There is an almost even division of opinion among medical men as to whether chlorine-treated water is, or is not, injurious in metabolism. One writer finds it beneficial in the treatment of such diseases as infantile diarrhea, and another argues that even very slight traces are injurious to the organism. There must be established, therefore, by careful research upon living organisms just what the effect of chlorine-treated water is, and what the maximum allowable concentration of the gas may be without serious consequences.

Before any adequate interpretation of such experiments can be made, however, it is necessary to know

¹ Brioux, *Ann. Sci. Agron.*, [3] 1 (1910), 241; Hovermann and Koch, *J. Landw.*, 64 (1916), 317; Pfeiffer and Simmermacher, *Landw. Vers.-Sta.*, 90 (1917), 415; Johnson, *Tid. Kemi, Farm. Terapi*, 15 (1918), 349; Cowie, *J. Agr. Sci.*, 9 (1919), 113.