# Some Factors Affecting the Fixation of Nitrogen as Sodium Cyanide<sup>1</sup>

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A study has been made of the effect of variations in the quality and proportions of the charge components, concentration of carbon monoxide gas in the nitrogen, temperature, and nitrogen excess on the rate of conversion and on the maximum conversion of sodium carbonate to sodium cyanide by heating a charge of sodium carbonate, carbon, and iron in nitrogen.

Silica in the charge lowers the maximum conversion by making sodium carbonate unavailable for cyanide formation in the ratio of  $2Na_2CO_3$  to  $1SiO_2$ .

It is found that the equilibrium conversion of carbonate to cyanide with nitrogen gas containing 30 per cent carbon monoxide is 64 per cent at  $950^{\circ}$  C. and with 50 per cent carbon monoxide is 67 per cent at  $1000^{\circ}$  C. These values confirm the measurements of Ingold and Wilson.

The cyanide-forming reaction is quite rapid if a large enough excess of nitrogen is used to keep the carbon monoxide concentration low. Thus experiments are shown in which 71 per cent of the sodium carbonate in a particular charge is converted to sodium cyanide in 15 min-

**P**OR almost a century there have been frequently recurring attempts to put upon a commercial footing the fixation of nitrogen as cyanide by heating a mixture of potassium carbonate, sodium carbonate, or barium carbonate and carbon (and iron as a catalyst in some cases) in a stream of nitrogen. In this country attention has been devoted almost exclusively to the use of sodium carbonate, for which case the reaction is represented by the equation

 $Na_2CO_3 + N_2 + 4C + Fe = 2NaCN + 3CO$ 

+ Fe-138,500 cal. (1)

Ammonia may be produced by the hydrolysis of the cyanide so formed, according to the equation

 $NaCN + 2H_2O = NaCOOH + NH_3$ 

The catalytic action of iron in Reaction 1 was discovered in 1839 by Thompson<sup>2</sup> and has recently been emphasized by Bucher.<sup>3</sup>

It has appeared that the cyanide process for nitrogen fixation would have some advantages over other known processes, in that (1) the temperature required is so low that fuel heating could be used, thus obviating the necessity for cheap electric power, such as required by the cyanamide and arc processes, and (2) the apparatus and technic should be simpler than that in the synthetic ammonia process with its high pressures or the cyanamide process with its high temperatures and its several process steps. These apparent advantages have led to renewed trials of one or another type of cyanide process in the face of a long list of past technical and financial failures, many of which have involved the loss of large sums of money. As an example of the optimism which has prevailed in some quarters, it may be recalled that in the early days of the participation of the United States in the World War estimates by reliable chemical engineers indicated that ammonia could be produced by the sodium cyanide process at a lesser cost than by any other fixation process. It was not until the

utes. It is hence evident that the long heating periods heretofore used could be greatly shortened if heat could be supplied to the charge more rapidly.

In order to minimize the retarding effect of carbon monoxide on cyanide formation, and hence to make possible a large per cent conversion with a reasonable excess of nitrogen, it appears that a temperature of at least  $1050^{\circ}$  C. should be used.

It was found that with increasing temperature the proportions of iron catalyst could be decreased. At  $1050^{\circ}$  C. 1 or 2 per cent of iron would appear to be sufficient.

The reactivity of metallurgical coke for the formation of sodium cyanide is much less than that of wood charcoal, petroleum coke, coconut charcoal, or lampblack.

Continued treatment of a charge in which the formation of cyanide is completed results in the distillation of material containing much metallic sodium, indicating that sodium cyanide is appreciably dissociated in the vapor phase. Sodium cyanide can, therefore, not be recovered from a crude charge by distillation.

erection of the U. S. Chemical Plant No. 4, at Saltville, Va., which was designed to produce 10 tons of sodium cyanide per day, that the difficulties in carrying out the process on a large scale were ascertained. While the results of the short trial run made at this plant before it was scrapped following the armistice were not an accurate index of the best that might be done with continued operation, yet they serve to dispel practically all hope of economically producing ammonia in a plant of the character of that at Saltville.<sup>4</sup>

Since that time the cyanide process of fixation has been generally regarded as of value only for the production of the relatively high priced sodium cyanide. One plant has now for a number of years been fixing nitrogen as cyanide in this country on a considerable scale,<sup>5</sup> the principal final product being liquid hydrocyanic acid.

The main difficulties encountered in the attempts to fix nitrogen as cyanides have been of an engineering character, arising chiefly from the necessity of heating indirectly a solid or somewhat plastic charge of low heat conductivity, in which an endothermic reaction is taking place. There was considerable uncertainty also regarding the maximum conversion obtainable, the rate of cyanide formation, equilibrium conditions, intermediate reactions, and similar points. This laboratory has studied this latter phase of the problem, the greatest amount of effort being expended in a determination of the intermediate reactions which lead to the formation of sodium cyanide, and a study of these relatively simpler reactions separately. Some of the results obtained have been or are soon to be published.<sup>6</sup> At the beginning of the investigations, however, considerable work was also done on the effect on the reaction as a whole, as summed up by Equation 1, of varying such factors as the quality of the materials used, the proportions of the ingredients in the

Chem. Met. Eng., 30, 368 (1924).
Brown, THIS JOURNAL, 11, 1010 (1919).

mitted for publication in J. Am. Chem. Soc.

<sup>6</sup> (a) Guernsey and Sherman, J. Am. Chem. Soc., **47**, 1932 (1925); (b) **48**, 140 (1926); (c) "The Thermal Dissociation of Sodium Cyanide," sub-

<sup>&</sup>lt;sup>1</sup> Received January 4, 1926.

<sup>&</sup>lt;sup>2</sup> Dinglers polytech. J., 73, 281 (1839).

<sup>&</sup>lt;sup>3</sup> This Journal, 9, 233 (1917).

charge, the purity of the nitrogenous gas, time of heating, temperature, etc. The present paper describes the results of some of these experiments.

In this investigation consideration has been given to the formation of sodium cyanide only, since it appeared that such a study would have more direct practical application in this country than one on either barium cyanide or potassium cyanide. Then again, no work was done on the hydrolysis of sodium cyanide to form ammonia, since this reaction seems of little practical importance until the costs of cyanide can be greatly reduced, and the problems connected with the hydrolysis appear less formidable than those involved in the production of cyanide.

A number of interesting papers in this general field have appeared within the last few years, and it seems desirable to list here a few of the more important of these. The stimulation of interest in the fixation of nitrogen as sodium cyanide in this country was largely due to Bucher,<sup>3</sup> whose work was published in 1917. Bartell<sup>7</sup> has described the work done by the War Department at Green, R. I., during the World War. Other papers of interest are those of Hara,<sup>8</sup> in which was demonstrated the high activity of iron catalyst prepared by decomposing iron salts in situ; of Morimoto,<sup>9</sup> and of Berl and



Braune,19 which appeared during the preparation of this manuscript. A complete bibliography of articles and patents dealing with the fixation of nitrogen as cyanide from the earliest experiments to July 1, 1924. has been prepared at this laboratory as part of a larger "Bibliography on Nitrogen. which is now available in card index form at the laboratory, and which it is hoped may be published later.

#### Apparatus and Method

The method of conducting these experiments was to heat a small quantity of an intimate mixture of sodium carbonate, carbon, and iron, usually in the form of briquets, in a measured stream of nitrogen or nitrogen and carbon monoxide, at a carefully controlled and measured temperature, for a def-

inite time, at the end of which the charge was chilled in an atmosphere of purified nitrogen. Analysis was made for total alkalinity by titration with sulfuric acid and for cyanide by the Lundell-Bridgeman<sup>11</sup> method, on the water extract of the charge and in many cases also on the alkaline sublimate

- <sup>10</sup> Fortschritte Chem., 18, Pt. 4, Series A (1925).
- <sup>11</sup> THIS JOURNAL, 6, 554 (1914).

which distilled from the charge into the cooler parts of the apparatus. Carbonate was determined in many experiments, and, in some, total and free iron.

The furnace was first raised to the desired temperature with the reaction tube, C (Figure 1), which is a 1-inch (25mm.) seamless steel tube, 14 inches (36 cm.) long, in place and nitrogen flow adjusted. The cap, E, carrying the iron pyrometer tube O (1/4 inch or 6 mm. O. D.), was then raised far enough to allow the briquets, H, to be dropped onto the perforated bottom of the reaction tube, C. The cap was then forced down tightly and the experiment timed from that point, although 5 to 7 minutes were required to bring the charge up to temperature. The temperature was controlled to within  $\pm$  10 degrees of the desired point. At the top of the charge it was about 10 to 15 degrees lower than that at the usual location of the chromel-alumel thermocouple junction, which was about 1 inch (25 mm.) above the bottom.

At the end of the time chosen for the experiment the cap and pyrometer tube were lifted out, any adhering material being knocked back into the reaction tube, and the reaction tube transferred as quickly as possible to a cooling tube standing alongside which had been previously filled with nitrogen and through which nitrogen was kept passing until the reaction tube and contents had cooled. At the same time an empty reaction tube was placed in the furnace in preparation for the next experiment.

As shown, the heated section of the apparatus is protected from oxidation by a stream of hydrogen injected through a small hole in the lower end of the furnace.

#### Materials

In all experiments a chemically pure grade of anhydrous sodium carbonate was employed. The carbon was supplied except where otherwise noted, as petroleum coke containing 1.8 per cent ash, of which 4 per cent was silica. The iron used in most experiments was purchased as an especially pure grade, and it was only after a great many experiments had been made that it was found to contain over 6 per cent silica. In a small number of experiments the iron was introduced as chemically pure magnetic oxide of iron obtained by burning pure iron in oxygen.

Unless otherwise stated, it is to be understood that all charges were in the form of cylindrical briquets, about  $\frac{1}{8}$  inch (3 mm.) in diameter by  $\frac{1}{2}$  inch (13 mm.) long, which were prepared by thoroughly mixing the three components (each through 200 meshes per inch), kneading with hot water, forcing through a die, and drying. During this process, the iron, if introduced as reduced iron, ordinarily became 40 to 60 per cent oxidized.

The nitrogen for the experiments was drawn from the usual compressed gas tank and purified by passage through a copper deoxidizer, a carbon dioxide scrubber, and a drying train, and finally through a bed of heated coconut charcoal in the lower part of the furnace tube (A, Figure 1).

### Results

The results of some of the typical experiments are shown in Figures 2, 3, and 4. It will be observed that the part of the total alkalinity of the charge which was due to cyanide—which will hereafter be referred to as "conversion"—does not approach 100 per cent, but passes through a maximum and falls again with continued treatment. Each point on the curve represents an average of one to seven experiments, the usual number being about three. When conditions were such that conversion was low the agreement between duplicate experiments was often poor. Since in a majority of experiments silica was present as an impurity, it will be necessary to consider first the effect of that substance on conversion.

<sup>7</sup> THIS JOURNAL, 14, 699 (1922).

<sup>&</sup>lt;sup>8</sup> Tech. Repts., Tóhoku Imp. Univ., 2, No. 1, 1 (1921).

J. Chem. Ind. (Japan), 21, 881 (1918).

March, 1926

EFFECT OF SILICA ON MAXIMUM CONVERSION—The maximum conversion is found to depend on the charge proportions and to be roughly the same at different temperatures with a given charge. At the lower temperatures this maximum was not reached because of the low rate of reaction. The failure to obtain conversions approaching more nearly 100 per cent in



Charge: 18 grams;  $Na_3CO_3$  1; Fe 2; C 3. Temperature, °C.: (1) 800; (2) 850; (3) 900; (4) 950; (5) 1000; (6) 900; (7) 950. In Curves 1 to 5 the flow of nitrogen was 0.2 liter per minute and in Curves 6 and 7 it was 0.5 liter per minute

these experiments was due largely to the combination of part of the alkali with silica introduced as an impurity, chiefly in the iron which contained 6.2 per cent. This was shown by adding definite amounts of silica to a charge made up with pure, finely divided magnetic iron oxide instead of the impure iron used in the experiments cited above, and noting the corresponding decrease in maximum conversion. As shown by Figure 5, the maximum conversion on the silicafree briquets is about 92 per cent as compared with about 76 per cent (Figure 4) for a similarly proportioned charge in which impure iron is used. With silica added to the magnetite charge in the same proportion in which it was present in the charges prepared from impure iron, the conversion dropped to 68 per cent. Additional proof of the formation of silicates was obtained by analyzing the water extract of the product of a number of experiments for silica. These analyses showed that practically the entire silica content of the iron and carbon entering the charge was in the watersoluble portion of the sample following treatment.

To account for the discrepancy between maximum conversion and 100 per cent on the basis of the combination of alkali with silica, it is necessary to assume that the combining ratio is  $2Na_2O$  to  $1SiO_2$ . Calculation of results on that basis shows good agreement, as is seen in Table I.

Table I—Effect of	Silica in	Charge	on 1	Maximum	$\mathbf{C}$	onversion
Charge proportions	{Na₂CO }Fe C	3 1 2 3	$\frac{1}{2}$	$\frac{1}{2}$	1 1 1	
Maximum conversion	Caled.	$5\overline{5}$ 49	$5\overline{6}$ $5\overline{6}$	57 7 59 7	76 76	$>^{89}_{72.5}$

Although the deleterious effect of silica has been repeatedly observed,<sup>3,5</sup> it is believed that no such quantitative relation between maximum conversion and silica content of the charge has been previously noted. Alumina would, no doubt, act in a manner similar to silica. It should be noted that the values for "maximum conversion" have no direct practical significance, since the proportion of impurities, such as silica, in a commercial charge will be different. As we shall see later, only a small percentage of iron catalyst will probably be used, thus decreasing the amount of such impurities from this source. On the other hand, unless the relatively scarce low-ash cokes are to be used, larger amounts of impurities will be introduced with the carbon than in the present experiments.

EFFECT OF CARBON MONOXIDE ON MAXIMUM CONVER-SION—The maximum conversion is limited by impurities in the gas, as well as in the charge. It may be seen from Equation 1 that, since carbon monoxide is a product of the reaction by which sodium cyanide is formed, the presence of carbon monoxide with the nitrogen should lower both the rate of conversion and the equilibrium conversion of sodium carbonate to sodium cyanide. The relation between the ratio of nitrogen to carbon monoxide in the gas and conversion has been studied by Ferguson and Manning<sup>12</sup> and later by Ingold and Wilson.<sup>13</sup>

A considerable number of experiments were also made in the present investigation on the conversion in the presence of carbon monoxide, using the apparatus and method described above. The results of some of these experiments are shown in Figure 6. The maximum indicated here should represent an approximate equilibrium condition. The depression in maximum conversion is, however, not entirely due to the carbon monoxide in the gas, but also, as we have seen, to the formation of sodium silicate from a portion of the alkali. For this particular charge the maximum conversion is about 76 per cent. If, then, 24 per cent of the alkali be considered as prevented by combination with silica from forming sodium cyanide, the "conversion" values shown in Figure 6 do not correctly represent the ratio of sodium cyanide to the total alkali available for the formation of cyanide, but this may be calculated. This calculation has been made and it may be seen from Table II that the corrected results agree more closely with those of Ingold and Wilson, than with those of Ferguson and Manning.

<sup>12</sup> This Journal, **11,** 946 (1919).

18 J. Chem. Soc. (London), 121, 2278 (1922).





Table II—Cyanide Process Equilibrium					
Temper- ature °C.	CO in gas mixture Per cent	Maximum conversion (cor.) Per cent	-EQUILIBRIUM Ferguson and Manning	VALUES Ingold and Wilson	
950 1000	30 50	64 67	42 56	$\substack{62\\68.5}$	

The results at  $1000^{\circ}$  C. with 30 per cent of carbon monoxide are not included in this calculation, since there is some doubt whether the maximum was reached in these experiments.

RATE OF NITROGEN SUPPLY AS A FACTOR LIMITING RATE OF CYANIDE FORMATION—It will be obvious from these equilibrium considerations that an excess of nitrogen over that





which becomes combined as cyanide must be used in order to keep the concentration of carbon monoxide which is formed below such a point that cyanide formation would be stopped. Since three volumes of carbon monoxide are formed for each volume of nitrogen absorbed (Equation 1), the excess of nitrogen which must be used is sometimes surprisingly large, particularly at the lower temperatures, since the equilibrium becomes less favorable to the formation of cyanide with decreasing temperature.

It appears, then, that the rate of cyanide formation may sometimes be limited by the rate of nitrogen supply, even though only a small fraction of the nitrogen passing is absorbed to form cyanide. This was not fully realized at the start of the present investigation, and many experiments were made aimed at determining the effect of miscellaneous factors on the rate of reaction where nitrogen supply was in reality the limiting factor. It is believed that this same mistake has been made in published investigations. It will be of interest, therefore, to present data which will give some idea of the stoichiometric excess of nitrogen necessary to keep the carbon monoxide concentration low enough to permit the reaction to proceed under different conditions.

It will be seen that in experiments where the conversion is limited by nitrogen supply, under identical conditions except as to the rate of nitrogen flow, the conversion should be the same after supplying a given number of equivalents of nitrogen irrespective of the time required to supply this nitrogen. The extent to which this condition is found to hold is shown in Table III.

Table III—Rate of Nitrogen St	upply as a	Factor Limiting	Conversion
COMPOSITION OF BRIDUET	TS	Duration	

			. Or DRI	20410		10 11 11 11 11		
			Fe	C (petro-	Mois N <sub>2</sub>	$N_2$		Conver-
	Parts	Parts	intro-	leum	per mol	treatment	Temp.	sion
Expt.	Na <sub>2</sub> CO <sub>3</sub>	Fe	duced as	coke)	Na2CO3	Min.	° C.	Per cent
1	1	1	Fe <sub>3</sub> O <sub>4</sub>	1	5.76	15	1000	45
<b>2</b>	1	1	Fe <sub>3</sub> O <sub>4</sub>	1	5.76	37.5	1000	42
3	1	1	Fe <sub>3</sub> O <sub>4</sub>	1	11.52	15	1000	71
4	1	1	Fe <sub>3</sub> O <sub>4</sub>	1	11.52	75	1000	71
5	1	1	Fe <sub>3</sub> O <sub>4</sub>	1	5,76	15	1050	58
6	1	1	Fe <sub>3</sub> O <sub>4</sub>	1	5.76	37.5	1050	65
7	1	2	Fe	3	10.94	15	900	26.5
8	1	2	Fe	3	10.94	37.5	900	39.5
9	1	<b>2</b>	Fe	3	10.94	15	950	31.5
10	1	2	Fe	3	10.94	37.5	950	42.5

It is seen that in those charges in which the iron was introduced as oxide the conversion for a given number of equivalents was not mainly dependent on time within the limits investigated. In those experiments, however, in which the iron was introduced as finely divided metallic iron, the conversion was somewhat lower in the 15-minute than in the 37.5-minute treatment. This may indicate that iron reduced in the charge, as in Experiments 1 to 6, is a somewhat more active catalyst than iron introduced in the metallic state, as in Experiments 7 to 10. It is possible, however, that this difference is due to the lower temperature in Experiments 7 to 10.

Experiment 3 of Table III is of interest from a practical standpoint in that it shows that the cyanide reaction is quite rapid and that a quite high conversion may be obtained in a very few minutes, provided carbon monoxide is rapidly removed. This serves to emphasize the fact, which has been recognized by most of those who have studied the problem, that the long times which it has been necessary to heat the charges in commercial installations in order to get satisfactory conversions have been due to the low rate of heat penetration into the charge, rather than to a low rate of reaction.

The data presented in Table III are of further practical importance in that they show what excess of nitrogen must be used under different conditions. They show that, unless comparatively high temperatures are used in order to shift the equilibrium toward cyanide, it is necessary to employ a very large excess of nitrogen in order to obtain a high conversion. With continuous retorts, with charge and nitrogen entering at opposite ends, and with charges containing only a small amount of iron oxide, the excess required would be somewhat less than under the conditions of the experiments shown in this table. Nevertheless, considering these and other data, it is believed that a temperature at least as high as 1050° C, should be used. This conclusion was also reached by Bartell.<sup>4</sup>

	Та	ble IV-	-Iron Cont	ent and l	Rate of Rea	action	
Expt.	Composit Parts Na <sub>2</sub> CO <sub>3</sub>	Parts Fe	BRIQUETS Parts C (petroleum coke)	Mols N2 per mol Na2CO3	Duration N2 treatment Min.	Temp. °C.	Conver- sion Per cent
123456789010	1 1 1 1 1 1	$1 \\ 0^{a} \\ 1 \\ 0^{a} \\ 1 \\ 0^{a} \\ 1 \\ 0^{a} \\ 1 \\ 0^{a}$	1 1 1 1 1 1 1	$12.30 \\ 12.30 \\ 4.61 \\ 4.61 \\ 9.22 \\ 9.22 \\ 4.61 \\ 4.61 \\ 6.92 \\ 6.92$	$\begin{array}{c} 80\\ 120\\ 30\\ 45\\ 60\\ 90\\ 30\\ 45\\ 45\\ 67.5 \end{array}$	$\begin{array}{c} 900\\ 900\\ 1000\\ 1000\\ 1000\\ 1000\\ 1000\\ 1050\\ 1050\\ 1050\\ 1050\\ 1050\end{array}$	$52 \\ 10, 5 \\ 54 \\ 30 \\ 74 \\ 45 \\ 69 \\ 61 \\ 73 \\ 70 \\ 70 \\ 10, 5 \\ 10$

<sup>a</sup> None added. Coke contained equivalent of 0.25 part.

VARIATION IN RATE OF REACTION WITH PROPORTION OF CATALYST IN CHARGE—With only a relatively small proportion of iron as a catalyst in the charge, the rate of formation of cyanide no longer keeps pace with the supply of nitrogen, as is shown in Table IV. The results show clearly the decreasing necessity for large proportions of iron as the temperature is increased. It would seem that at temperatures of  $1050^{\circ}$  C., or more, such as appear to be required by the equilibrium conditions, 1 or 2 per cent of iron in the charge would be sufficient.

VARIATION IN RATE OF REACTION WITH KIND OF CARBON USED<sup>5,7</sup>—A series of experiments with different forms of carbon under parallel conditions gave the following conversion: with wood charcoal, 32 per cent; petroleum coke, 31 per cent; coconut charcoal, 28 per cent; lampblack, 30 per cent; metallurgical coke, 1.2 per cent. It is possible that in these experiments the nitrogen supply was insufficient to distinguish small differences in the reactivity of the first four kinds of carbon, but it is perfectly clear that the reactivity of metallurgical coke is much below that of the other forms. This very much lower reactivity was observed in all experiments in which metallurgical coke was used.

CHARACTER AND AMOUNT OF SUBLIMATE FROM CHARGE-Since the entire charge of these experiments is at a practically uniform temperature, materials volatile at the temperatures employed passed out of the charge and condensed in the cool top part of the reaction tube. Since in most experiments the briquets remained firm and did not adhere to the reaction tube, the washings from the tube after the briquets were removed represented little except sublimate. Without showing the detailed results thus obtained, it will suffice to say that in most of the experiments in which the treatment was not continued beyond the time necessary to obtain maximum conversion, the volatilization loss was of the order of 10 per cent or less. The sublimate consisted largely of sodium carbonate in many cases more than 75 per cent of the total alkalinity being due to that substance. This was probably distilled for the most part as sodium cyanide or metallic sodium and converted to sodium oxide and carbonate by the action of carbon monoxide and dioxide in the gas. The average proportion of cyanide in the sublimate was about



18 per cent, while the proportion present as neither carbonate nor cyanide—presumably as sodium oxide or metallic sodium —was on the average about 21 per cent.

The volatilization from the charge became much more marked under certain conditions. Thus, when the relatively unreactive form of carbon, metallurgical coke, was used, or when the proportion of iron catalyst in the charge was very low, sodium was produced more rapidly than it could be converted to cyanide, and was deposited with the sublimate. Similarly, higher rates of gas flow tended to carry metallic sodium into the sublimate. (In all cases where metallic sodium was found, there was also a small amount of sodium carbide, as indicated by the very distinct odor of acetylene obtained on moistening the sublimate.) Again, the observation was repeatedly made that on too long continuation of the treatment of a charge with nitrogen, the volatilization



rate increased rather abruptly at a certain point, corresponding probably with the building up of the cyanide concentration in the top layers of the charge. The following experiment illustrates what takes place when a charge is heated in a flow of nitrogen for too great a length of time.

A quantity of briquets was nitrified and well mixed. The nitrified briquets contained 37.65 per cent total alkali, of which 80 per cent was combined as sodium cyanide. This was the maximum conversion obtainable with that particular kind of briquet. Portions of this nitrified sample were then heated to 1000° C. for varying lengths of time in a flow of nitrogen at 0.2 and 0.5 liter per minute, respectively. After each experiment the briquets were removed from the reaction tube and a separate examination made of the briquets and of the sublimate which condensed in the cool end of the reaction tube. The results are shown in Table V.

Table V—Decomposition of Cyanized Briquets in a Nitrogen Atmosphere—Temperature 1000° C.

		-BRIQ	UETS	•		
		Original				
		alkali	"Con-	REACT	ION TUBE W	ASHINGS.
		remain.	version"	PERCE	NT ORIGINA	T ATRAIT
Time	N <sub>2</sub> flow	ing	Per	As	As	In other
Hours	T /min	Domont	aont	NON	Nacon	forme
110415	L./ 11111.	rercent	cent	-vac.v	1 a2003	Torms
0.5	0.2	85	77	4.6	5.0	3.9
1	0.2	81	77	5.3	8.4	5.7
1.5	0.2	72	76	8.3	10.7	9.4
2.5	0.2	51	77	9.7	15.8	19.7
3	0.2	60	71	7.4	15.0	11.6
3	0.5	10	25	3.6	18.3	52.6

The significant fact to be noted is that only a small part of the alkali disappearing from the briquets appears in the sublimate as sodium cyanide. That the alkali in "other forms" was largely metallic sodium was evidenced by the vigorous hydrogen evolution and explosions on washing out the reaction tubes. This can be explained only by the fact that at this temperature sodium cyanide is appreciably dissociated in the vapor phase. It is evident from this that the proposal which has appeared repeatedly in the patent literature to recover cyanide from the crude furnace product by distillation is not feasible. A detailed study has been made of the equilibria at different temperatures between sodium cyanide and its dissociation products and the results are being published elsewhere.<sup>60</sup>

## **Soluble Silicates**<sup>1</sup> Their Influence on Hypochlorite Bleach

### By John D. Carter

That silicates of soda increase the efficacy of the

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SILICATES of soda have long been used to improve the bleaching power of hydrogen peroxide. Weber<sup>2</sup> found that oxygen was lost less rapidly, and in smaller quantities, when silicates were used to make the bath alkaline than when other substances were so used. This treatment he found to be not only superior, showing more even bleaching, but considerably more economical.

hydrogen peroxide bleach has long been established. The present investigation shows they are equally effective when used in hypochlorite bleaching. Their usefulness is expressed by their effect on the

potency of the hypochlorite solutions themselves; the effect on bursting strength of the fabric; the increase in ash content of the fabric due to a deposition of silica, probably in hydrous form; and their marked ability to render cheesecloth and sulfite pulp brighter and whiter than when bleached with hypochlorite alone.

The most alkaline commercial grade of silicate of soda is the most effective.

The present work was undertaken in order to determine whether silicates have the same beneficial action with hypochlorites as that displayed when they are added to the peroxide bleach.

### Instability of the Solutions

Titrations with arsenite solutions showed that the potency of the hypochlorite decreased when the solution was allowed to stand exposed to the air, and to some extent, even when kept in stoppered glass bottles. Silicate added to the solution seemed neither to hasten nor retard this action (Table II). It also failed to show any effect when in the presence of such inert materials as bleached wood pulp or cheesecloth (Table III). This was true for both sodium and calcium hypochlorite. But when a bleachable material—for example, sulfite pulp—was present, the silicate of soda very distinctly conserved the bleaching power of the solutions, as shown by Table IV. Not only was two to ten times as much available chlorine found remaining after given periods of time and exposure, but in every case in which silicate of soda was used the colors of the pulps were better than in corresponding tests without silicate. In many cases the color secured by the use of a little silicate of soda was better than could be obtained by the use of any amount of hypochlorite solution used alone.

In studying the effects of hypochlorite solutions, with and without the addition of silicate of soda, cheesecloth was selected as representing cotton textiles, and three grades of sulfite pulp as representing that class of paper stock. The effect of various treatments on the strength of the cloth was traced by determining the bursting strength as shown by the Mullen tester. Averages of a number of tests were taken in

<sup>2</sup> J. Soc. Dyers Colourists, 39, 209 (1923).

nate the variations always to be found in such materials. Effect on Strength of Fabric

every case in order to elimi-

It has long been known that treatments with hypochlorite solutions might weaken the fabrics.<sup>3</sup> This was confirmed by a series of tests in which the concentration of the solutions, their temperature, and the dura-

tion of the treatment were varied. As was to be expected, the loss in strength was proportional to the severity of the treatment. The addition of silicate of soda reduced considerably the loss in strength, as shown by Figures 1, 2, and 3. During the first 15 minutes there is even a slight gain in strength when silicate is used. Figure 1 represents more nearly actual laundry practice than do Figures 2 and 3.

	Table I—Silic	ates Used in t	he Various Tests	i i
No.	Na2O Per cent	SiO2 Per cent	Mol. ratio	• Bé
$\frac{1}{2}$	$10.5 \\ 19.4 \\ 0.10 \\ $	$\begin{array}{c} 26.7\\ 30.6\\ \end{array}$	1:2.60 1:1.62	42 58.8
3 4	13.7	29.0 32.9	1:3.53 1:2.56	41 52

The pieces of cloth to be tested were carefully weighed in order that a uniform humidity might be maintained. The cloth was cut in rectangular pieces and measured as accurately as possible both before and after treatment. Considerable shrinkage was noted in every case. Treatment with water at 50° C. for 10 minutes followed by drying in the air produced contraction of 4.9 per cent in area and a consequent apparent gain in strength of 16.7 per cent. With 2 per cent of sodium carbonate in the water the contraction was 4.6 per cent and the apparent gain in strength 7.1 per cent. As noted above, treatment with hypochlorite solution weakens the cloth. This treatment caused shrinkage which normally results in increased strength. But the weakening effect of the hypochlorite was greater than the gain due to shrinkage, so there was a net decrease in strength.

Two series of tests were made, repeating the treatments fifty times in each. Parts of the test pieces were cut off at intervals and used for the determinations of ash content (Figure 4). In the first series the pieces were put through

\* Tailfer, "Practical Treatise on the Bleaching of Linen and Cotton Yarn and Fabrics," translated by McIntosh, p. 137. Scott, Greenwood & Son.

<sup>&</sup>lt;sup>1</sup> Received October 31, 1925.