

ORIGINAL PAPERS

THE FIXATION OF NITROGEN¹

By JOHN E. BUCHER

The herein described process for the fixation of nitrogen differs primarily from all those now in commercial use in fixing nitrogen in the form of alkali cyanides instead of in the form of oxides of nitrogen, calcium cyanamid, nitrides, or ammonia. It is further characterized by operating at very moderate temperatures such as 900 to 950° C. so that it is not dependent upon cheap electric power and, it can, because of this moderate temperature, be operated in iron retorts. It is of the utmost simplicity, uses iron, which is the cheapest metallic catalyzer, and does not require pure materials such as nitrogen but can use air or producer gas just as well. It requires no special apparatus and can hence be operated at once with what can be found in practically every manufacturing community. It does not require skilled labor to operate it, and it is preëminently a method which can be installed quickly in an emergency for the preparation of cyanides, ammonia and nitric acid.

These statements are based on a very large amount of chemical and engineering work, most of which was done three to five years ago, and which has appeared only in the form of patents from time to time. I have not heretofore published anything regarding any part of this work.

Meanwhile certain circumstances arose which made it necessary to abandon my work on nitrogen fixation and abnormal political and industrial conditions have affected our country as well as the rest of the world. I think that all thoughtful people agree that we are in no position to face any serious crisis which might suddenly arise.

For example, we are now practically in the midst of an alkali cyanide famine which is causing very serious hardships in a number of our industries and our Government officials estimate that we would need 180,000 tons² of nitric acid per year in case of war with any first-class power and that it is of the utmost importance to have some ready means of getting this from atmospheric nitrogen so as not to be dependent on the hazardous expedient of importing it by ocean transportation in the form of sodium nitrate from South America.

The popular idea seems to be that it is necessary to have cheap hydro-electric power to provide such quantities of nitric acid together with a costly plant which would require considerable time for its construction.

The data already accumulated in my work show that electric power is not necessary and that the process can be installed in a short time on any scale desired and at comparatively small expense. I had not intended to publish anything on my nitrogen fixation work for a few years more until I could complete

¹ Presented before the 9th Annual Meeting of the American Institute of Chemical Engineers, New York, January 10 to 12, 1917.

² Landis, *Transactions of the American Electrochemical Society*, **29** (1916), 83.

some further important engineering work connected with it. The above considerations, however, led me to the conclusion that I could not in justice delay action any longer, and hence your kind invitation to present this paper was accepted with the hope of completing the work as opportunity offers.

HISTORICAL

The fixation of nitrogen in the form of alkali cyanides is by far the oldest of all such methods and its first period of great commercial activity dates from 1840 to 1847 when it terminated in failure. In January, 1839, there appeared an abstract of the work of Lewis Thompson¹ on "Improvement in the Manufacture of Prussian Blue" with the statement that he had been awarded the Gold Isis medal of the Society of Arts in the previous year for this work. After speaking of the wasteful process of producing cyanides from animal matter then in use, he says:

"Reflecting on these circumstances, it occurred to me that the atmosphere might be made to supply, in a very economical manner, the requisite nitrogen, if allowed to act on a mixture of carbon and potash under favorable circumstances. The experiment proved on trial to be correct, and in some measure exceeded my expectation, for the carbonaceous matter employed may be worked over again many times, and is even improved by each operation. I found it necessary to use iron, for a reason which will be apparent in the explanation of this process: when iron is not employed, a much higher temperature is required."

He ground two parts potash, or pearl-ash, two parts coke and one part iron turnings into a coarse powder and heated the mixture in an open crucible in an open fire to a full red heat for about half an hour, stirring the mass occasionally. He obtained an abundant yield of cyanide which he converted into Prussian Blue.

I regard Thompson's remarkable work as the most basic that has ever been done on the fixation of nitrogen by the cyanide process. He discloses clearly the idea of using the nitrogen of the atmosphere and also states with the utmost clearness that iron is "necessary" in the process if it is to be carried out at a temperature short of "much higher" than a "full red heat."

Thompson's article soon led to very active discussions or investigations throughout the scientific world by some of the most noted investigators of the time, such as Berzelius,² Erdmann and Marchand,³ Fownes and Young,⁴ Langlois,⁵ Rieken,⁶ Delbrück,⁷ and Bunsen and Playfair.⁸

Practically all took the perhaps justifiable view

¹ *Mechanics' Magazine*, No. 822, May 11 (1839), p. 92; also *Dingler's polytechnisches Journal*, N. F. 23 (1839), 281.

² Berzelius, *Jahresberichte*, **21** (1842), 80.

³ Erdmann and Marchand, *J. prakt. Chem.*, **26** (1842), 412.

⁴ Fownes and Young, *J. prakt. Chem.*, **26** (1842), 407.

⁵ Langlois, *Ann. chim. phys.*, [3] **1**, 117.

⁶ Rieken, *Dingler's poly. Jour.*, **121** (1851), 286; *Liebig's Annalen*, **79** (1851), 77.

⁷ Delbrück, *Jahresberichte*, **1** (1847), 473.

⁸ Bunsen and Playfair, *J. prakt. Chem.*, **42** (1847), 392; Report of the British Association, 1845.

that Thompson had not proved the fixation of nitrogen because it might have come from the coke and some of those who did experimental work then prepared charcoal from sugar and heated it with alkali carbonate in a current of nitrogen. They all omitted the iron turnings and hence either obtained no cyanide, or only traces, or else had to heat it to a very high temperature. They finally concluded, however, that nitrogen could actually be fixed in this manner but that the favorable conditions for fixation were not known.

Commercial work began in 1840 and in 1843 Newton¹ took out the first patent for the formation of cyanides from atmospheric nitrogen. Works were finally located at Newcastle-on-Tyne which regularly produced over one ton of yellow prussiate of potash per 24 hours at a cost of 1.86 francs per pound, by drawing air down through retorts filled with charcoal containing potassium carbonate. These processes completely ignored Thompson's recommendation of the uses of iron and consequently had to be operated at a white heat. This caused poor yields, slow action, much loss of alkali, great expense in constantly renewing the refractory clay retorts which were speedily destroyed by the alkali and the process resulted in great loss of money and failure in 1847.

Since this numerous other attempts have been made to get cyanides from atmospheric nitrogen by methods which in the vast majority of cases did not use iron as a catalyzer. In 1881 to 1885 Victor Alder² of Vienna took out a series of patents in Germany and elsewhere. In the first of these he states that alkali carbonates can be converted into cyanides when heated to redness with carbon in nitrogen and that the process is essentially favored by the presence of metals such as finely divided iron, but that the use of iron is not an indispensable condition as the process succeeds completely even without its use. In a second patent he states that the combination takes place copiously only in the presence of gases containing carbon (hydrocarbons, carbon monoxide, or a mixture of the two) in which metals that are able to transmit carbon, such as iron, manganese, chromium, nickel, and cobalt act extraordinarily favorably as will be shown below. These, together with his other statements made in his patents, constitute such a mixture of truth and falsehood that it is not surprising that failure resulted after six years attempt to work the patents in Germany.

Thompson's original disclosure of the necessity of iron was finally so completely ignored or forgotten that Castner,³ who used alkali metals instead of carbonates, stated that iron is "inert" while Acker,⁴ who also used alkali metals, disclaimed iron as a "reactive" metal in the cyanide synthesis.

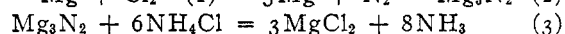
In view of these complete contradictions and the complete failure of the fixation processes depending on the formation of cyanides it is hence not surprising that development took place along the lines of elec-

trical fixation methods such as the arc and Cyanamid processes as soon as the production of large quantities of cheap hydro-electric power was accomplished.

EXPERIMENTAL

I—MAGNESIUM NITRIDE PROCESS

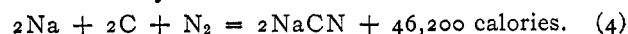
The above hasty study of nitrogen fixation to cyanides did not seem very encouraging and I did not have access to the work of Thompson and Alder at the time. Accordingly some work was done with nitrides with a view to fixing nitrogen according to the following equations:



This process was electrolytic in nature and was designed to affect improvements in the ammonia-soda process. The magnesium chloride would be electrolyzed to magnesium and the resulting metal would be burned in the nitrogen from the towers to fix nitrogen as magnesium nitride. This later would be heated with ammonium chloride obtained from the mother liquors to produce ammonia and regenerate the magnesium chloride for the electrolytic stage. This would greatly modify the ammonia-soda process by fixing its waste nitrogen, recovery of all the waste sodium chloride, elimination of waste liquors containing calcium chloride and the production of chlorine as a new product. It depends, however, on cheap electric power and would depend upon being operated in connection with the ammonia-soda works. As I wished to get a general nitrogen fixation process which was not dependent upon any locality or industry, this work was abandoned.

II—NITROGEN FIXATION WITH ALKALI METALS

The decision was now made to test the chemical principles upon which the fixation of nitrogen to cyanide depended and it was decided to use free alkali metal at first to study the reaction:



An apparatus shown in Fig. 1 was accordingly con-

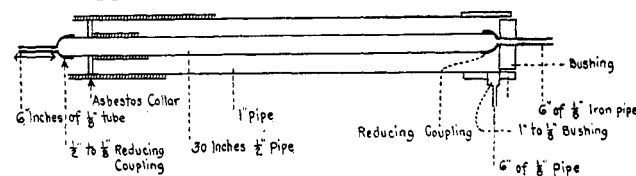


FIG. 1

structed of an ordinary 1/2-in. malleable iron pipe about 30 in. long, connected at both ends with a reducing coupling and with 1/8-in. inlet and outlet pipes. This 1/2-in. pipe was then placed inside of a larger outer pipe which had a tee and bushings at one end and a ring of asbestos board at the other. This apparatus gave a means of heating in a combustion furnace while the inner tube was surrounded by an atmosphere of hydrogen or nitrogen to prevent oxides of carbon from diffusing through the walls of the inner tube and forming sodium carbonate with the metallic sodium. Hydrogen diffuses into the inner tube so easily that, with a slow current of nitrogen and a 2-ft.

¹ Bertelsmann, "Die Technologie der Cyanverbindungen," Berlin (1906), p. 85.

² *Ibid.*, pp. 90-91.

³ Castner, U. S. Patent 577,837 (1897).

⁴ Acker, U. S. Patent 1,019,002 (1912).

section red hot, the exit gas at the end of the tube burned and contained about 200 cc. of hydrogen per hour. Carbon monoxide diffuses very much more slowly and was detected with iodine pentoxide.

EXPERIMENT 1—The inner tube was then filled with lampblack containing substantially no ash and the whole heated in a current of hydrogen to a white heat, cooled, opened, and then 14 grams of sodium added at one end and a current of nitrogen passed into the inner tube. Reaction began slowly and continued for three days (25 hours), the current of gas being occasionally reversed to drive sodium vapor first one way and then the other.

The tube was cooled, opened and found to contain perhaps 0.5 gram of unchanged metallic sodium. The tube and contents were washed with water and gave 23.7 grams of sodium cyanide which is 79 per cent of the theory based on the quantity of sodium used.

In another case the inner tube was charged with 80 grams of electrode graphite, powdered to pass through a 100-mesh sieve, and ignited with a current of hydrogen for over one hour. Then it was cooled, 12 grams of metallic sodium were added and then it was heated in a current of nitrogen for 2¹/₂ days (about 20 hours) to redness as above and 58 per cent of the theoretical amount of cyanide was obtained.

Quite a number of experiments of this nature were made and while the absorption of nitrogen was sometimes faster than at others, it was always a matter of hours. There is hence no question that cyanide formation is slow under these conditions.

EXPERIMENT 2—I now decided to try my idea that iron should act as a catalyzer notwithstanding the above assertions to the contrary. A ¹/₂-in. iron tube was hence heated as before while a current of nitrogen was passing, after being charged with 120 grams finely powdered alcoholized iron, 12 grams of ignited lampblack and after 7 grams of metallic sodium had been pushed into the charge.

When the tube got to a low red heat, absorption of nitrogen began so rapidly that a partial vacuum was formed and the water through which the exit gas bubbles started to rush back towards the hot iron tube and was stopped only by quickly turning on the nitrogen in a torrent. The absorption was practically instantaneous and there was no time to take observations. Only a small quantity of exit gas bubbled through the water and it must have been argon. The whole thing was finished just as soon as the requisite nitrogen could be passed in and 94 per cent of the sodium was converted into cyanide. The absorption was exceedingly sharp and the end of the tube was entirely free from carbon and contained a core of porous iron of a bright silvery luster and so malleable that it flattened out under a pestle.

There were sintered globules of metal showing that the temperature must have risen hundreds of degrees higher inside of the tube than outside owing to the powerful exothermic nature of the reaction. This experiment shows with the utmost sharpness that:

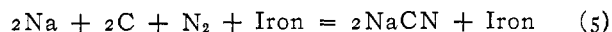
(1) Iron is an exceedingly active catalytic agent in the fixation of nitrogen.

(2) The reaction is powerfully exothermic.

(3) We have a new method for the preparation of argon.

(4) The reaction gives a fine method of separation of nitrogen and the argon group in gas analysis.

We may now write the equation thus:



Suspecting that much of the slow absorption in Experiment 1 was due to the walls of the iron tube, the experiment was repeated by forcing a thin seamless copper tube into the inner ¹/₂-in. iron tube. This tube was charged with 4 grams of sodium and some ignited lampblack and heated in a current of nitrogen for 4 hours. No absorption could be noticed and on titration it was found that only 10 cc. of nitrogen had been converted into cyanide. This shows very sharply the catalytic influence of the walls of iron tubes.

III—PURIFICATION OF IRON

The above Experiment 2 and the equation shows that while we are dealing with the fixation of nitrogen with sodium, carbon and iron, we are necessarily removing carbon from the charge and hence purifying the iron. Sodium in the form of solid, liquid or vapor, has frequently been added to iron and so has nitrogen. Sodium and nitrogen have even been added separately or alternately to the same mass of iron. But I have found no disclosure wherein any one even hinted at treating iron with sodium and nitrogen simultaneously so as to remove the carbon in the form of cyanide by virtue of the catalytic action of the iron itself.

This seems to be a novel process which is just as interesting as the nitrogen fixation itself. It depends upon a powerfully reducing action while all large commercial processes depend upon the oxidizing action for the removal of carbon. It cannot attack the iron after the carbon is removed as is the case in oxidation reactions. It will remove not only carbon, but also sulfur, oxygen and phosphorus. It suggests the idea of removing silicon and manganese by the oxidation processes even to the extent of overburning the iron and then removing the remaining oxides, carbon, sulfur and phosphorus with sodium with or without the previous addition of carbon and that a Bessemer converter might be blown with nitrogen and sodium vapor. It also leads one to wonder whether with very cheap sodium it could not be made to apply to iron from ores very rich in phosphorus.

To further test these ideas for solid iron, a number of hacksaw blades were heated to redness in nitrogen and sodium vapor for a number of hours. They came out very soft and silvery in appearance and could not be tempered, thus showing that the carbon had disappeared and that the iron had acted as a catalyzer to purify itself. This removal of carbon, sulfur, and phosphorus must take place substantially instantly at the surface of the iron and it is hence determined practically by the rates of the diffusion of these substances through the hot iron.

The removal of carbon from a piece of steel wire is so complete that when the latter is made the anode in dilute hydrochloric acid, it remains bright and there

is not the slightest sign of carbon as the iron dissolves. If desired the surface of the iron can be purified quickly and the interior will remain in the form of steel. Many interesting topics arise regarding the electrical properties of iron thus purified, corrosion of iron and the coating of the metal with tin, zinc, etc., but their discussion would require a separate paper.

IV—PREPARATION OF METALLIC SODIUM

The general principles of physical chemistry regarding the reversibility of chemical reactions at once led me to consider whether the above reaction for the decarburization of iron might not be reversible and that it might hence be written:



You will at once notice that this is simply the equation for the case-hardening of iron by means of cyanides which has been known for a long time. In fact, it is practically evident that when the iron takes the carbon from sodium cyanide, it must set free the other two elements, sodium and nitrogen, which do not recombine under the conditions at which case-hardening takes place. This hence gives us a new method of getting metallic sodium based simply on the process of case-hardening iron with the additional precaution of keeping away air or gases which would destroy the liberated metallic sodium. With all the practical use of cyanogen compounds in casehardening, it is curious that no record of such a disclosure for preparing sodium could be found.

EXPERIMENT 3—Accordingly some sodium cyanide was mixed with pure iron powder in an iron tube and heated. A considerable layer of metallic sodium was found in the colder part of the tube. Similar experiments with potassium cyanide gave metallic potassium quite readily.

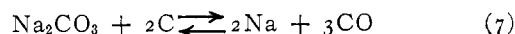
The same thing happens when the cyanide is added to molten iron and this might be of special interest practically because the carbon could be removed from the molten iron by a current of air blown into the converter and cyanide then passed in again as before. The general method of operation would be very similar to that used in making water gas commercially.

I did not follow this up because I had no suitable means for testing the engineering features of such a process and the method of getting sodium by the electrolysis of cyanide with the incident formation of cyanogen, oxamide, oxalic acid and formic acid, which will be described later, seems to offer greater advantages than this new method.

V—NITROGEN FIXATION WITH ALKALI CARBONATES

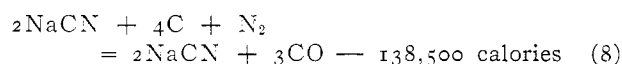
Having now determined that iron, or some similar element, was an exceedingly efficient as well as essential catalytic agent in the fixation of nitrogen, I decided to test the following ideas:

At a given temperature which is quite high, sodium carbonate and carbon give the reaction



which was formerly used for the preparation of sodium. It would hence seem that at moderate temperatures

of, say, from 860 to 980° C., we might get traces of metallic sodium according to the equation. This free sodium should then react practically instantly with the carbon and nitrogen, providing finely divided iron were present as has already been shown. If these ideas are correct, we should get an extraordinarily cheap and efficient method of nitrogen fixation, providing the reaction velocity for the formation of metallic sodium vapor is high. This would mean that as the sodium vapor disappeared to form sodium cyanide, more sodium would immediately be liberated, according to the law of mass action, to re-establish the equilibrium and the process would thereby become continuous, and we could represent it thus:



The following two experiments support these views in the most striking manner:

EXPERIMENT 4—In this experiment a mixture of 10 grams of finely powdered graphite was heated with 5 grams of sodium carbonate from 920 to 940° C. for 50 minutes in a current of nitrogen. A 1/2-in. copper tube was used in order to avoid the catalysis of iron walls. At this temperature there was a very slow but steady evolution of carbon monoxide and some white fumes passed out of the tube with the gas current. These fumes imparted a steady but not very intense yellow color when they were led into a Bunsen flame. Upon cooling, a minute quantity of free metallic sodium was found in the end of the copper tube. This hence gives positive experimental evidence that the formation of metallic sodium from carbonate takes place according to the above equation at temperatures below 940° C.

The contents of the tube were lixiviated and tested for cyanides with iron salts in the usual way. No precipitate of Prussian blue formed even on standing for a few minutes and only a slight greenish blue color showed no more than a trace of cyanide to have been present.

A similar experiment was then made with 30 grams of finely divided iron and 5 grams of sodium carbonate in a slow current of nitrogen for 50 minutes at 920 to 1000° C. In this test the issuing gas did not impart the slightest color to the Bunsen flame, thus showing that no sodium was formed and that the carbonate is so slightly volatile as not to give a flame test under the conditions of the experiment.

EXPERIMENT 5—A mixture of 10 grams of graphite and 10 grams of finely powdered iron with 5 grams of sodium carbonate was now heated in a 1/2-in. iron tube from 920 to 940° C. for 50 minutes in a current of nitrogen, just as in the preceding experiment in which no powdered iron was used. There was a steady flow of gas which burned with the characteristic blue flame of carbon monoxide. The escaping gases showed no fumes nor did they at any time show the slight yellow color.

The product showed a conversion of over 60 per cent sodium carbonate into sodium cyanide and a very heavy precipitate of Prussian blue was obtained.

These two experiments establish the foundation for nitrogen fixation in the sharpest possible manner and they support the above quotation of Lewis Thompson's work in the most striking way. They show that at a red heat we can have no nitrogen fixation with carbon and soda ash alone, but, that when finely divided iron is added, we have an exceedingly efficient method.

These experiments, which cost practically nothing and took only a few hours' time, were made in 1912 and they emphasize the utter inexcusability of those who quoted Thompson's invention and then ignored his positive statement about the necessity of the presence of iron for work at a red heat. They also show that Alder's above-mentioned statement, that the fixation of nitrogen at a red heat succeeds even without the presence of iron, etc., is entirely erroneous and that his claim that "carbonizing" gases, such as carbon monoxide, must be introduced with the nitrogen if cyanides are to be formed abundantly, has not the slightest basis in fact.

It shows at once that, by ignoring the work of Thompson, investigators and manufacturers were forced to work at such exceedingly high temperatures that the results could be only a ruinous destruction of apparatus and commercial failure.

The above facts are in harmony with Dr. Ewan's statement in his carefully prepared article in Thorpe's "Dictionary of Applied Chemistry," Revised Edition, Volume II, 1912, page 196:

"A few temperature measurements which the writer made with a platinum rhodium thermocouple showed that potassium vapor is first evolved from a mixture of potassium carbonate and charcoal at about 1350° and that the formation of cyanide takes place very slowly at this temperature, the potassium cyanide volatilizing for the most part."

These experiments, together with Dr. Ewan's temperature measurement, show why even the methods which used alkali metals *without catalyzers* were doomed to failure as well as those using alkali carbonate. It is of no use from the technical point of view to work on any method which involves conditions under which material suitable for apparatus will not stand up. I had this sharply in mind when I determined to get a cyanide fixation process which should be effective at say from 860 to 950° C. so that iron or copper apparatus might be used in carrying out the process. The addition of the iron catalyzer solved this problem, which I regard as the most important in my entire work, so completely, that, judging by Dr. Ewan's figure, the temperature of cyanide formation is lowered more than 500° C.

I made hundreds of experiments with powdered carbon in the form of charcoal, coke, lampblack, etc., and with sodium, potassium, caesium, rubidium, and barium compounds in the form of carbonates and hydroxides to test various points under widely varying conditions and to get quantitative data for technical application.

Ultimately a series of tests was made with the powdered materials in horizontal iron tubes of varying sizes which ultimately reached 6 in. in diameter and

10 ft. in length. Time will not permit the description of these experiments and tests. I can say that only the best results were obtained with 2-in. pipes, 10 ft. in length. In some of these cases equal portions of the solution, lixiviated from the cyanized charge, required the same number of cc. of $N/10$ $AgNO_3$ solution, acidified with nitric acid, and of $N/10$ H_2SO_4 (with methyl orange) for titration.

These figures show all the alkali metals to be present as cyanides, and this is what I mean when I speak of cyanide of 100 per cent purity. When such a solution is evaporated to dryness *in vacuo*, it is easy to obtain a residue directly which titrates for over 95 per cent of sodium cyanide.

BRIQUETTING

Having thoroughly established the general conditions for efficient nitrogen fixation with substances in powder form, the next thing was to work out engineering methods for handling the materials. The inconvenience of heating powder in a current of nitrogen gas at a red heat, naturally suggests briquetting. A study of the art reveals numerous examples of briquetting, usually done with such substances as tar, pitch, resins, etc., or by use of lumps of charcoal, wood, and like substances to attain the desired porosity.

Desiring to avoid the use of such foreign substances, I first prepared briquettes by heating the mass of sodium carbonate, coke and iron to the melting point of soda ash in the absence of air. The pasty powder upon slight pressure becomes compacted and yields briquettes which are very hard and compact upon cooling. I have found such briquettes to be quite active, and they gave cyanide of 100 per cent purity upon being heated for 10 minutes in a current of nitrogen.

This is a fascinating process since the briquettes would already be at a cyanizing temperature just as they are formed. It would, however, mean the solving of unique engineering problems; hence I did not follow it further at the time.

The experience with the red-hot briquettes led me to conclude that perfectly satisfactory briquettes could be made by adding hot water to the mixed charge of coke, soda ash, and iron, and making use of the solubility curves and transition points of the phases of sodium carbonate as shown approximately in Fig. 2.

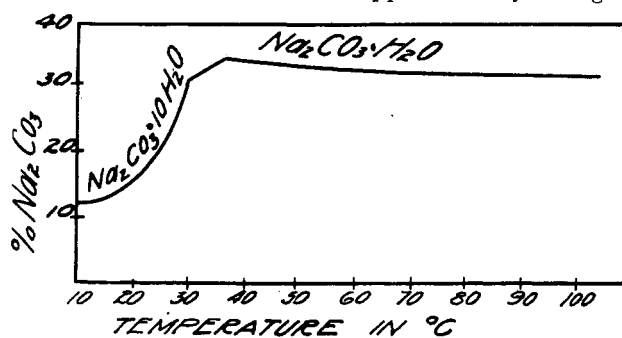


FIG. 2

The curve at a glance shows that the mass should be mixed with the water at as near the maximum temperature of 104.75° as convenient. We shall

then have a mixture of monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, coke, and iron moistened with a hot saturated solution of sodium carbonate. These phases cannot change on cooling until the temperature reaches about 35°C ., at which the crystals would take up all the water and we would later have a dry hydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, as far as the water added would permit.

In other words, there is here a range of fully 70°C . through which the mass might cool before the briquetting operation would be interfered with. These predictions were realized in an exceedingly satisfactory manner, and many tons of briquettes were prepared without the slightest trouble. At first an ordinary concrete mixer without steam jacket was used. The hot water and the heat of hydration of the soda ash brought the temperature (work done in the summer) high enough to give fine briquettes, but as the temperature was not much above the transition point, the whole mass had a tendency to set like plaster of Paris if the operations were delayed.

Later a steam-jacketed kneading machine was used with the utmost convenience so that the full length of the monohydrate curve was available before cooling could stop the process. The hot, dough-like mass was briquetted with an ordinary small power-driven meat chopper having a cylindrical worm with a steel disc of $3\frac{1}{2}$ in. diameter and having 37 circular holes of $\frac{1}{8}$ in. diameter. The knife was fixed so that the briquettes were cut off at about 1 in. length. The efficiency of these small machines was surprising, *e. g.*, the 9-gal. steam-jacketed kneading machine gave 7200 lbs. of briquettes per 24 hours with 15 minutes to the charge, and it could just as well have been run at 5 minutes to the charge to give 21,000 lbs. of briquettes per 24 hours. The meat chopper, which was smaller than that often seen in a city market, easily gave 5,000 lbs. of briquettes per 24 hours with inexperienced help, and I have been able to force it to three times this capacity for a short interval. Thus even a few of these machines not much larger than toys would give a very large yearly output. Of course, a large brickmaking machine would give a very large output commercially.

These briquettes should be dried rapidly so as to get them hard and free from dust. Hot waste gases are very satisfactory for such drying. A commercial bake-oven would dry many tons per day or a dryer can be constructed out of brick and iron very quickly. If the briquettes cool before they are sufficiently dry they will harden, and, on further standing, will fall to powder as one might expect when the bulky hydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, forms to break them up just as freezing water may break a spongy, brittle substance. I have dried briquettes in the hottest part of the Bunsen flame in less than two minutes.

The powder was prepared for this work on a commercial scale by grinding iron scale (magnetite, haematite, etc., will do just as well) to a 100-mesh powder in an iron ball mill with manganoid steel balls; then an equal weight of coke previously ground in a similar way to 100-mesh was added and the grinding continued for

perhaps an hour; then the soda ash was added and the grinding continued for 5 minutes or even less.

The iron or iron scale and coke, being solids, must be mixed with the utmost thoroughness, but the soda ash becomes mobile by addition of water in briquetting as well as by fusing at 860°C . in the furnace so that no great care is necessary in mixing it with the other two constituents. Briquettes thus prepared with iron scale gave as high as 28 per cent of NaCN in the heated charge. Thus it is shown that we may start with iron oxides instead of metallic iron. In the first run we may thus produce finely divided iron which is in very fine condition for subsequent runs.

I will hereafter, for convenience, speak of the surface of carburized iron which is in close contact with the ground carbon as the "catalytic solution surface." For cyanide formation it is only necessary to have nitrogen, sodium carbonate, and such a catalytic solution surface in contact simultaneously. It is, hence, evident that sodium carbonate in too large quantity will flood the solution surface so that the nitrogen cannot get at it readily. This will smother the reaction so as to make it sluggish, and it is, thus evident that there must be a percentage of soda ash which will give maximum commercial efficiency.

The three following experiments were made to give a rough quantitative idea of this factor: They were made with 50 lbs. of alcoholized iron and with 50 lbs. of pulverized coke ground for 5 hours in the ball mill and the mixture was then briquetted with three different proportions of soda ash.

EXPERIMENT 6—In this case the iron-coke-soda ash was briquetted in the ratio respectively of 2 : 2 : 1 so as to give a 20 per cent soda ash briquette. Then 150 grams of these briquettes were heated in a 1-in. iron pipe in a current of nitrogen at a temperature from 600 to 1000°C . The reaction took place briskly and the issuing gas burned finely. The briquettes were cooled, lixiviated and titrated in the manner described above. They were found to contain 13.7 per cent of actual NaCN corresponding to 85 per cent of the total alkali metal in the solution. For brevity, I shall speak of such cases as 85 per cent purity.

EXPERIMENT 7—Here the same materials were briquetted to make a 1 : 1 : 1 iron-coke-soda ash ratio and 150 grams were heated as before in the 1-in. horizontal iron tube at a temperature from 600 to 1030°C . for 30 minutes. The gas evolution was considerably slower than in Experiment 6. The resulting briquettes contained 20 per cent of actual NaCN of 95 per cent purity.

EXPERIMENT 8—In this case the iron-coke-soda ash mixture was made into 1 : 1 : 2 briquettes which contained 50 per cent of soda ash, and 150 grams were heated in the same horizontal iron pipe in the nitrogen current for one hour at 600 to 1090°C . The combustible gas evolved sluggishly during the entire time, and the mass finally contained 14 per cent of actual cyanide of 80 per cent purity.

These three experiments show that the 20 per cent soda ash briquettes were quite reactive, the 33 per cent ones intermediate, and the 50 per cent one rather

sluggish so that they had to be heated longer and to a higher temperature in order to get the poorer result. These experiments rather indicate that with either larger or continuous acting furnaces it should be easy to get cyanized briquettes to contain at least 30 to 35 per cent of actual NaCN and this prediction was later verified. The experiments also clearly show the loss of alkali compounds by volatilization during the run.

If the briquettes do not completely fill a horizontal pipe, or, if they sag somewhat, as inevitably they must as soon as they become plastic when soda ash melts, then the nitrogen will tend to pass through the upper channel rather than through the briquettes. This is further aggravated by the counter-current of carbon monoxide which is formed in the reaction.

This factor is not very serious in a $\frac{1}{2}$ -in. pipe or even a 1-in. pipe, but it must become more serious with larger diameters. The following two experiments give conclusive data on this point.

EXPERIMENT 9—Twenty-five pounds of the same 2 : 2 : 1 briquettes such as were used in the 1-in. pipe in Experiment 6 were heated in a horizontal 6-ft. piece of 6-in. iron pipe and the temperature kept from 1000 to 1080° C. for 1 hour and 20 minutes while a current of nitrogen was passing.

Upon cooling it was found that the plastic charge had sagged $\frac{1}{2}$ in. in the upper part of the tube to produce a crescent-shaped channel as shown in Fig. 3.

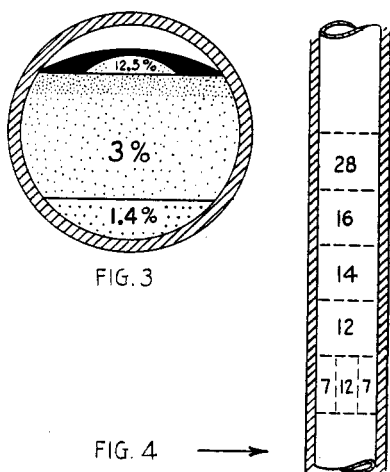
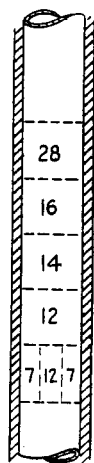


FIG. 4 →



The entire charge averaged only 3.5 per cent of actual NaCN of very low purity as against 13.7 per cent cyanide of 85 per cent purity under the far milder and shorter treatment of the same sample of briquettes in the 1-in. horizontal pipe in Experiment 6. A vertical section at about the middle of the charge was also tested and it showed 12.5 per cent cyanide in a narrow top layer, then 3 per cent in the broad intermediate layer, while the bottom layer showed only 1.4 per cent NaCN. This is also shown diagrammatically in Fig. 3.

EXPERIMENT 10—The result in the preceding experiment showed that increasing the size of a horizontal pipe to 6 inches, when the current of nitrogen passed into the end, completely ruined the process commercially. If this theory is correct, then this damage could be avoided entirely by placing the pipe vertically.

This was done with the same 6-ft. pipe of 6 in. diameter, and as I had no more of the 2 : 2 : 1 briquettes on hand, we used the more sluggish 1 : 1 : 1 briquettes as a 50-lb. charge.

The pipe was heated from 1000 to 1090° C. for only 1 hour and 10 minutes with a rapid current of nitrogen passing. This gave a massive column of yellow flame which at its maximum arose to a height of 4 to 5 ft. above the mouth of the vertical 6-in. shaft.

On cooling, the top of the charge was found to contain 24 per cent of actual NaCN while the bottom contained 20 per cent, giving an average for the entire charge of 22 per cent, and showing that over 10 lbs. of cyanide must have been produced in this run.

These two spectacular runs on a semi-commercial scale show at a glance that my process can be absolutely ruined by simply placing the retort horizontally in the furnace instead of vertically.

The same thing was also shown with longer and larger pipes in which the charges were on a scale of hundreds of pounds of briquettes in each run.

EXPERIMENT 11—This run was made in the same vertical pipe of 6 in. diameter as had been used in the preceding Experiment 10. It was made to test the volatility of the alkali compounds quantitatively: The charge happened to be 55 lbs. of briquettes consisting of 22 lbs. of iron scale, 24 lbs. coke and 9 lbs. of soda ash. The heating continued for 2 hours at 1000 to 1100° C.

Upon cooling, the top layer of briquettes was found to contain 28 per cent of actual NaCN of 87 per cent purity. Passing down, the other sections showed, respectively, 16, 14, 12 and 10 per cent of actual NaCN and the purity of the four sections varied from 90 to 93 per cent.

The lower section contained a central cone of moderately firm briquettes whose content was 12 per cent of NaCN of 100 per cent purity. This cone was surrounded by an annular section which had fallen to powder because its content of 7 per cent sodium cyanide was no longer enough to hold the particles of iron and carbon together.

These results are shown diagrammatically in Fig. 4, and they show exactly the general results we should expect in an experiment of this sort where we have heat passing in through the walls of the tube and a rapid gas current sweeping through the hot briquettes exposing a large surface for the evaporation of alkali compounds. The endothermic reactions in this case intensify the effect.

This experiment at once suggests two methods of solution, both of which I have carried out successfully in practice. The first would be to make the briquettes so active that they could be cyanized at lower temperatures, thus reducing the loss by volatility very greatly and by making other suitable changes. The other solution would be a continuously operating furnace, and here great volatility would be a most valuable asset.

ACTIVITY OF BRIQUETTES

The two following experiments were made with 25 grams of briquettes heated in each case in a current

of nitrogen in a $\frac{1}{2}$ -in. iron tube which was laid horizontally into the heat zone of the furnace.

EXPERIMENT 12—In this case 2 : 2 : 1 iron-coke-soda ash briquettes were used. They were heated from 710 to 920° C. in 13 minutes. There was an exceedingly rapid evolution of carbon monoxide which died down to almost nothing in 6 minutes before a temperature of 900° was reached. The product contained 15.2 per cent of actual NaCN of 92 per cent purity. We may, hence, conclude that 2 : 2 : 1 briquettes should give over 15 per cent cyanide of over 90 per cent purity in 10 minutes at temperatures below 920° C.

EXPERIMENT 13—In this case the alkali was washed out of the briquettes and soda ash then added directly to the moist filter cake of iron and coke so as to make 1 : 1 : 1 iron-coke-soda ash briquettes.

These briquettes did not give the rush of carbon monoxide which was noted in the preceding experiment, but there was a steady evolution of gas during most of the 28 minutes while the tube was being heated from 620 to 920° C. There was still some action when the heating was stopped.

The resulting briquettes contained 30 per cent of actual NaCN and the purity was 87 per cent. This very satisfactory experiment shows that we can get over 30 per cent cyanide of 87 per cent purity in a batch furnace below 920° C. in less than 30 min. heating. We may, hence, conclude that an efficient nitrogen fixation takes place below 920° C.

In another experiment briquettes from the same lot of 2 : 2 : 1 iron-coke-soda ash briquettes used in Experiment 12 were heated for 10 minutes from 560 to 820° C. and gave 11.5 per cent of actual NaCN of 61 per cent purity. This shows that even below 820° C. we get considerable quantities in a few minutes. The process can, hence, certainly be carried out at very reasonable temperatures.

This reaction could easily be carried out in copper tubes which do not oxidize easily. It also shows that at mines the cyanide could be lixiviated and the moist filter cake could be treated with soda ash in the kneading machine, briquetted, and used over again.

CONTINUOUS FURNACES

The second way of overcoming the loss of alkali noted under Experiment 11 is to have the charge moving continuously, preferably by gravity; this would keep the final concentration of alkali in the briquettes just the same as at the beginning, because, whatever distilled from the heat zone would necessarily have to return to it and, hence, would be of advantage in insuring contact rather than a disadvantage.

This type of process would have great advantages in many other ways, some of which will be pointed out. The process would act very much like a blast-furnace but it would differ in yielding a plastic product instead of molten products.

The first experiment was carried out with an 8-in. iron pipe, 8 ft. long, placed vertically in a furnace and connected by means of a tee with a worm conveyor immediately below the furnace. Everything worked well for a while until the hot plastic briquettes

got into the conveyor and hardened so that it could not be turned. This was rather what had been expected; therefore, the experiment was modified by using a tube 14 ft. long so that the worm conveyor could be placed about 4 ft. below the bottom of the furnace. Fig. 5 shows the principle of the arrange-

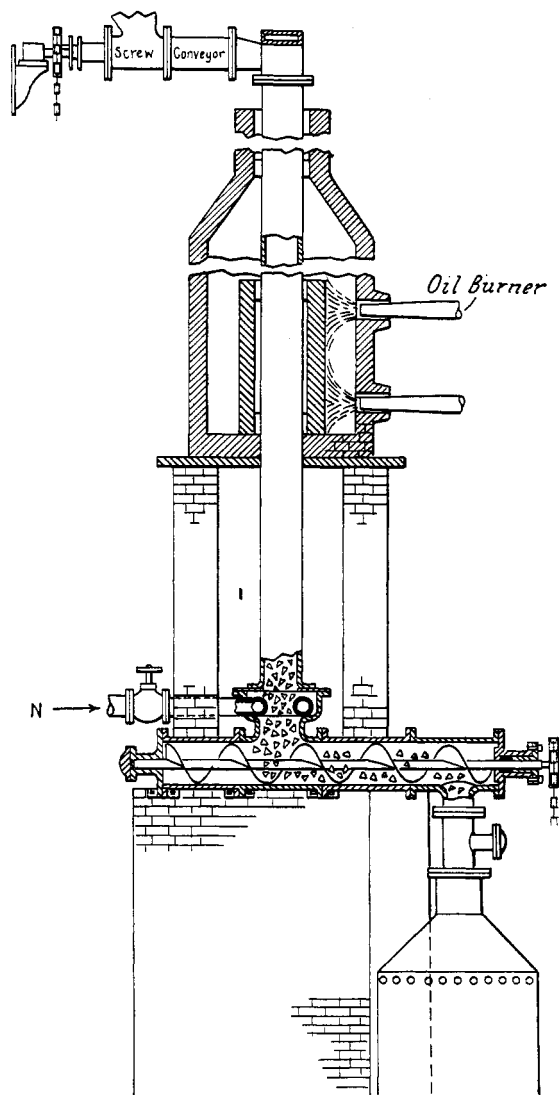


FIG. 5

ment. Here the descending, incandescent, plastic briquettes would cool by the ascending current of nitrogen, and by the air outside. The cooling was made more thorough still by using a current of water and a piece of cloth wrapped around the pipe below the heat zone. In this way the briquettes became cooled and hardened so that they passed through the conveyor in about the same physical condition as that in which they entered the furnace.

The hardened briquettes, however, stick in the pipe so that hammering may be necessary to move them, and at times when the pipe was rough it gave much trouble. This can be helped in various ways, such as making the entire pipe conical, or by making only that part below the heat zone conical, by making the briquettes larger, by feeding briquettes poor in alkali in the annular ring next to the wall of the pipe, or

even, pieces of coal or coke might be fed into the outer annular space while the core of the charge contained the briquettes richer in alkali, or, the cooling zone might be a larger pipe than that used for the heat zone as shown in Fig. 6. A complete solution would no doubt be obtained by making the cooling zone so wide that the hot cyanized briquettes would have to cool below the solidifying point of the sodium cyanide before they could come in contact with the iron walls.

The idea is well shown in Fig. 7 where the hot plastic

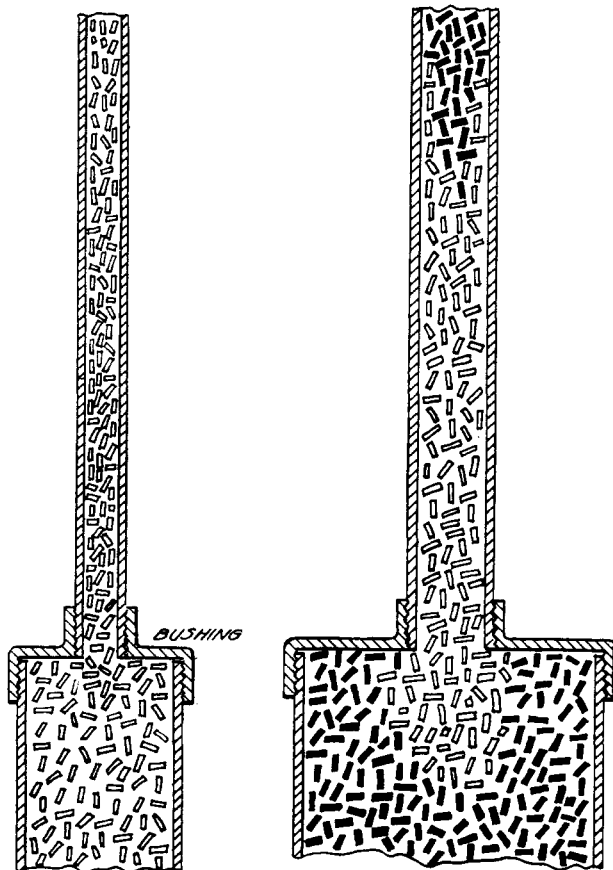


FIG. 6

FIG. 7

briquettes are shown not shaded while the cooler hardened briquettes are shaded. I have never had the hot plastic briquettes stick in a furnace operated according to my directions; the sticking always took place after they had hardened. Also, solid briquettes never stick in a properly operated furnace.

This very simple principle shown diagrammatically in Fig. 7 can, hence, scarcely fail to remove this difficulty absolutely. There is a slight tendency to stick at the top of the heat zone where the briquettes are just softening, but I have also been able to obviate this with the utmost ease by observing certain conditions.

In some of the work I made tests in a vertical iron pipe 22 ft. long and 8 in. in diameter. This required 500 lbs. of briquettes to charge it and then, in some tests, 3,000 lbs. were fed in a 24-hr. run.

The furnace was constructed on an improved principle as compared with that shown in Fig. 5. The furnace consisted essentially of a double chimney

with a thin partition separating the two compartments. An oil burner flame was directed vertically down one flue and the flame then led around baffles into the other flue which contained the 22-ft. pipe. The flame then passed up around the pipe and by controlling the draft at the top an effective furnace was obtained.

I further led a number of air jets into the main flue in such a way that the air oozed through long, narrow slits into the burning gases. In this way a reducing combustion could be maintained in the heat zone and the entire length of pipe in the furnace could be heated to a perfectly uniform temperature when desired. The whole furnace was within a derrick-like structure high enough so that burned-out pipes could be hoisted out mechanically without cooling them, and new ones inserted. Considering that these were simply first crude attempts, the furnaces worked surprisingly well. I believe that they are practical and that a gas producer would do the work far more easily, but, unfortunately, I did not have one—hence, the oil burner furnaces.

AN ELECTRIC FURNACE

When the price of yellow prussiate of soda and red prussiate of potash began to rise and ultimately reach values of \$7.00 and \$28.00, respectively, for each pound of nitrogen they contained, I decided to construct two types of electric furnaces which depended on the principles I had in mind for years in case of emergency either at the mines or for these chemicals. It was self-evident that they would work and that they could be installed in a few hours where any sort of commercial current is available. They depend simply upon using iron as a resistor and then keeping away oxygen so that they cannot burn out.

The first one was merely a piece of 1½-in. galvanized iron pipe such as is used on buildings as a water conductor. Two strips of copper were clamped about the ends for leads and the whole tube set vertically in a chimney of brick which were piled on the floor to give an opening 9 inches square. The space between the galvanized pipe and the brick were filled with magnesia asbestos and the furnace was complete. It was filled with briquettes and the currents of nitrogen and electricity were turned on. The zinc burned off like a flash and in a very few minutes there was a steady uniform heat in the briquettes and a fine flame of carbon monoxide. The transformer gave only 350 amperes and I had no means of measuring the voltage which was probably not over 2 or 3 volts. Resulting briquettes contained over 22 per cent NaCN.

Wishing to carry out this exceedingly satisfactory experiment quickly on a larger scale and being unable to get a suitable transformer, I purchased a small 15 kilowatt welding machine for the emergency. These machines are rated at 2 or 3 volts for the secondary current and only 50 to 75 per cent efficiency because they are light and intended only for intermittent service.

The furnace was now made from a piece of ordinary

4-in. iron pipe, 6 ft. in length. This was thrust through an iron drum about 4 ft. high and thirty inches in diameter with round holes for the iron pipe. The leads from the transformer were connected to the pipe by

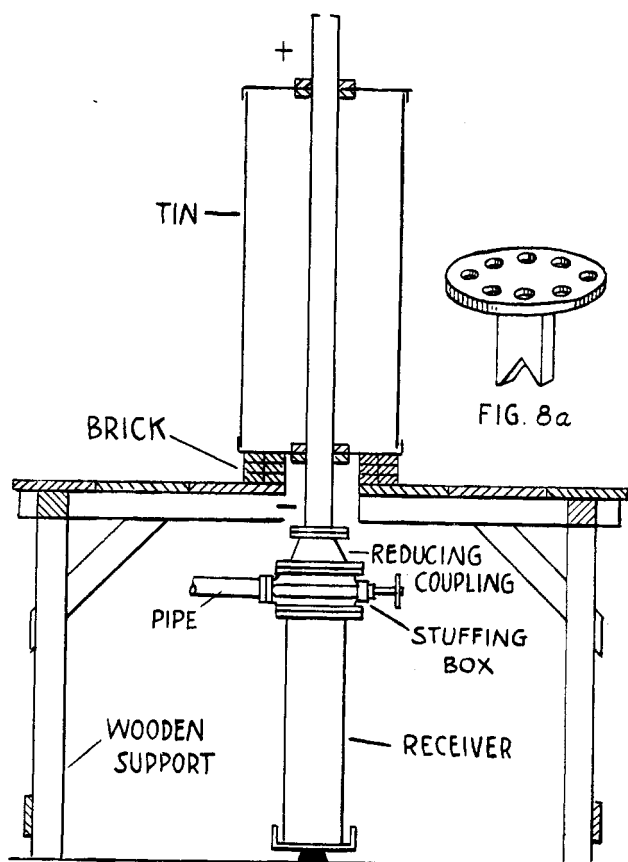


FIG. 8

strips of copper which had a cross-section of 3 in. by $\frac{3}{4}$ in. The drum was then filled with magnesia asbestos and the whole furnace was complete. Then an 8-in. to 4-in. reducing coupling was provided at the bottom of the 4-in. pipe and this in turn connected to a 4-ft. length of 8-in. pipe which was closed with a cap at the bottom. A hole for a 1-in. pipe was then drilled through the top of the reducing coupling and at one side there was a stuffing box for the $\frac{3}{4}$ -in. iron rod which held up the charge. The other end of this rod was supported by a piece of 1-inch iron tube which served as nitrogen inlet as well. Fig. 8 shows the furnace diagrammatically. A piece of fire-brick was now cut and fastened to another perforated round piece as shown in Fig. 8a. This was lowered into the furnace to support the column of briquettes.

The current available was not over about 9 kilowatts and this was turned on. After several hours the pipe had not become quite red hot but the machine and the copper leads were unduly heated. Accordingly a number of buckets of snow and ice were thrown over the leads and the welding machine. When the cloud of steam cleared away it was found that the iron tube was now at a good low red heat and it became hotter gradually.

The treatment with snow and ice was continued

through all the runs as it raised the efficiency by lessening the resistance of external circuit. Briquettes were now added and a fine run made, but it took 3 hours because the temperature was not as high as it should have been. Even so, I had no trouble in getting charges which gave 25 per cent of actual NaCN consistently. When the runs were finished a cap was turned on the top of the 4-in. pipe and the iron rod supporting the charge withdrawn. The entire charge dropped into the lower 8-in. pipe. The iron rod was now pushed back, the top opened and a new brick support lowered into the furnace and 15 lbs. of briquettes poured in.

The whole change took less than 2 minutes and the electric current was not shut off. The top was now closed again without interrupting the currents of electricity or nitrogen, the 8-in. pipe was removed, a new pipe substituted and the run proceeded as before.

The current was kept on this for about 3 days and a considerable number of runs made. The iron drum should be of thin metal to reduce reduction currents. It was so satisfactory in every way that I considered it unnecessary to run it any longer. This furnace, hence, avoids both sticking of the charge and if the drum is kept tight, or, a little nitrogen or reducing gas passed into the magnesia asbestos, it will be impossible for the pipe to be destroyed by oxidation.

By using a large number of pipes in series it would not even be necessary to provide a transformer, since we could allow a drop of a few volts for each pipe. If one has a three-phase current of, say, 125 volts at 120 amperes, it is possible to modify the furnace shown in Fig. 8 by merely setting a few fire-clay tiles 2 ft. high by 12 in. inside diameter around the 6-in. iron pipe which I used in this case. I allowed 3 pieces of $\frac{1}{8}$ -in. iron wire each 30 ft. long shaped as shown in Fig. 9 to hang down into the annular space between the tile and the pipe.

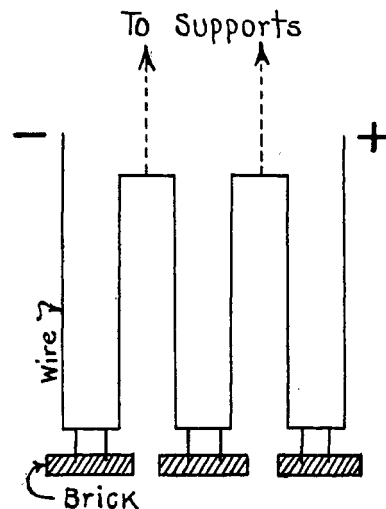


FIG. 9

There were 3 pieces of fire-brick at the bottom to keep the wires spaced from each other and from the iron pipe. The three segments were then used with

Y-connection and I was thus enabled to get 18 H. P. in the furnace instead of 12 by a single phase.

A slow current of nitrogen carrying some gasoline vapor, was passed into the annular space to prevent oxidation of the thin white-hot wire. This worked finely and gave over 30 per cent of NaCN in the briquettes used. The wire, even with this imperfect construction, lasted 9 hours, while it probably would not have lasted 9 minutes if air had been admitted.

On a large scale this furnace would be very simple since we would use only a single phase to each furnace and also use the furnaces in series and we would soon have to use say 1-in. iron rods for the resistors even with fairly high voltages such as 250 to 500. This entirely practicable type of furnace would probably be less desirable than that described already where the pipe itself is the resistor, but, in small scale work, it can be connected at once to any city current without expense of loss of time in waiting to have special low-voltage transformers made.

The resistance of iron increases probably 5 or 6-fold in heating from the room temperature to the cyanizing temperature, and varies with carbonization, etc. I have not been able to make strictly accurate observations, but in all of my work I found that the following formula gave me sufficiently accurate results so that the field rheostat regulation gave me entire control over the current.

$$\text{Amperes} = \frac{500 \text{ VW}}{L^2}$$

where V is the voltage used, W the total weight of iron in lbs. and L the total length of the conductor. I found it to hold for $\frac{1}{16}$ -in. wire, and for rods $\frac{1}{2}$ in. in diameter as well as for pipes from 1 to 4 in. in diameter.

These electric furnaces are not what I should intend to install if I were asked to put up a large plant but they are what I would put up for an emergency plant (to which I will again refer) because I have personally worked through every phase of these processes and nothing whatever is left to chance or guess work. The time factor would in such a case be more important than the greater economy and speed which I feel can almost certainly be obtained by internal electrical heating where the briquettes themselves are the resistor.

While we are speaking of the application of electrical heating with solid catalytic solution surfaces, it may also be well to mention the experiment with molten iron.

Fig. 10 shows the apparatus and is almost self-explanatory. It represents a cylindrical furnace with basic lining and a perforated bottom like a Bessemer converter. It contains molten iron into which coke or graphite fragments are deeply pressed. The graphite column acts as electric resistor to produce the heat and, while in the bath, it serves both to retard the gas bubbles so as to insure sufficient contact and to keep the iron saturated with dissolved carbon.

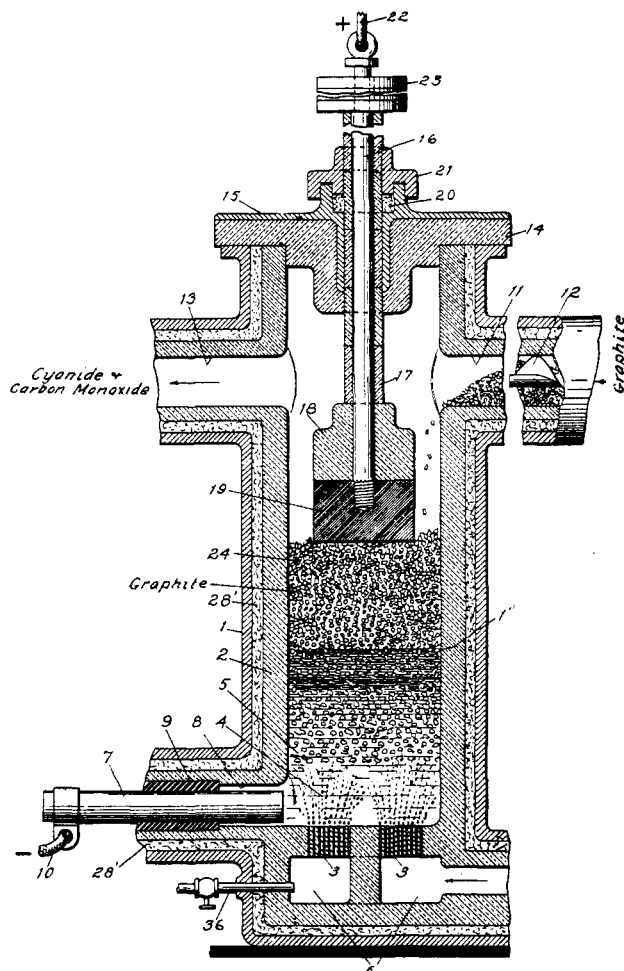


FIG. 10

Sodium vapor and nitrogen are blown into the bottom of the furnace and cyanide distils out at the top with the argon. The linings I used in the short time of the run stood better than I had expected. If the lining will stand sufficiently in actual work then I feel that ash in the carbon will be the other serious factor since the method of getting ashless carbon mentioned hereafter will not apply. However, there are other methods of solution.

RATE OF HEAT PENETRATION

In considering the technical application of these inventions, the rate of heat penetration into the briquettes becomes very important. The following experiment enables us to form some idea of the magnitude of this factor.

EXPERIMENT 14—In this run a 4-in. vertical pipe of iron was used with a pyrometer inserted in the center of the 8-lb. charge of the 2 : 2 : 1 iron-coke-soda ash briquettes through a $\frac{1}{2}$ -in. iron tube. The whole was placed in a cold furnace and a powerful oil flame used in the heating. By the time the outer pyrometer read 1030° C. the inner one in the charge read only 150° C. After 40 minutes more the outer one reached 1080° C. while the inner one registered only 880° C. In another 20 minutes the inside temperature read 1010° C. while the outer remained constant at 1080° C.

The heat, hence, flows in slowly and the rise is influenced by many factors of which the heat absorption of 138,500 calories is one. The result was 17 per cent of NaCN of 99 per cent purity in the briquettes.

This experiment gives the valuable data which enables us to say that it would take quite a while to heat a 6 or 8-in. column of briquettes to a uniform temperature. It also seems to confirm the very probable idea that the charge will conduct much better after it is partially heated than when it is cold. The importance of both these observations will be shown later.

INTERNAL ELECTRICAL HEATING

Experiment 14 shows that this factor would seriously retard rapid working in cyanide formation with large masses where the heat had to penetrate in from the outside. It would be a question of hours in large tubes. If we could use the charge directly as a resistor and thus generate the heat within the briquettes themselves, the heating would be reduced from hours to minutes with proportional saving of radiation losses and increase of output. Experiments along this line are very hopeful and wonderfully interesting, and I think no similar thing has ever arisen in electrical furnace work. To discuss adequately the very important results already obtained would require more time than is available for this entire paper, and I am not yet at liberty to disclose the most important of them.

I am, hence, compelled to dismiss this with the following general statements: The briquettes contain an insulator, soda ash, which makes them practically non-conductors at the room temperature but the conductivity increases very rapidly until at cyanizing temperatures it may easily increase 3,000-fold. It is, hence, only necessary to heat the charge to start the current or to put the briquettes into a hot furnace. I have heated a charge in a glass tube with the current in a few seconds so that the entire run was finished in less than 1 minute with abundant yield of cyanide and I have also heated charges of many lbs. in a few minutes. This suggests wonderful possibilities and shows that here is an entirely different proposition from that discussed in the case of the electric furnace shown in Fig. 8.

AIR INSTEAD OF NITROGEN

Having now shown how to fix nitrogen with simple apparatus with pure nitrogen, I desired to get away from the use of pure nitrogen so that my process would not be tied up to ammonia-soda or similar works, where nitrogen is a waste product. Also I did not wish to be compelled to put up a liquid air or other plant in order to get nitrogen. I suspected from the fact that carbon monoxide is formed in large quantity in the process, that a little more would do no harm under the right conditions. This suggested at once the use of producer gas in place of pure nitrogen or even the use of air directly providing it passed through hot coke before it reached the catalytic solution surface.

A number of runs were, hence, made in horizontal iron pipes of 1 in. diameter as shown in Fig. 11.

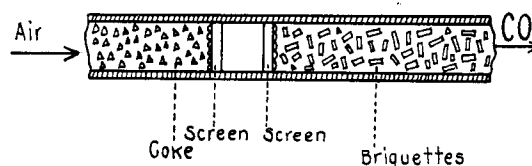


FIG. 11

Several inches of layers of coke were held in position in the tube with iron screens and then another screen kept the briquettes away from the porous absorbing surface of the coke. The pipe was heated to the cyanizing temperature and a current of air then passed in. Of course, this gave an extra fine carbon monoxide flame. When the process was over the air was shut off before the tube was cooled.

Similar runs were made in the apparatus by using pure nitrogen and the results were just the same as when air was used. In other cases the producer gas was made in a separate furnace and then passed into the cyanizing tube.

There was no apparent difference in any of these results. It is, hence, evident that the process is independent of pure nitrogen and that air, producer gas, flue gas, or even the gases from the combustion chamber of the furnace could be drawn through the cyanizing tube just as well. To make the test still more striking on a commercial scale, two pipes of iron 8 ft. long were put side by side vertically in a furnace as shown diagrammatically in Fig. 12.

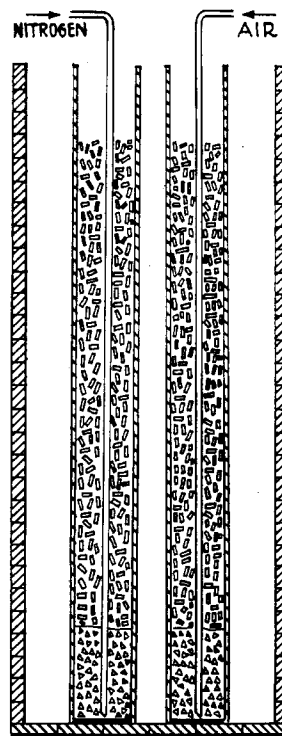


FIG. 12

One pipe was 6 in. in diameter and as I had no other of this size, the other was taken of 4 in. diameter. The

pipes were closed with caps at the bottom and then iron pipes of $\frac{1}{2}$ in. diameter were thrust to the bottom of the larger pipes and about a foot layer of coke was dropped into each one. Then 72 lbs. of briquettes were poured into the larger pipe and an equally deep layer was placed in the 4-in. pipe.

The whole apparatus was now heated red hot for a considerable time and pure nitrogen passed into one and air into the other. The result was 19 per cent of NaCN in the pipe which had the air and 18 per cent in that through which the pure nitrogen passed. These results are practically identical, thus showing that air can be used and that the process can now be operated anywhere. You can now see how easily producer gas could replace the nitrogen in working the electric furnace shown above in Fig. 8.

PRODUCTION OF NITROGEN

Although I do not need nitrogen in my fixation process with carbonates, it is, nevertheless, very convenient to have it for tests and when working with the alkali metals themselves. The passing of air over heated copper has many great advantages, particularly in the fact that the reagent is solid. Notwithstanding this, there seems to be much prejudice against it commercially and it was condemned as impractical or impossible just as many of the other basic things I have described to-night.

As no one cited any physical or chemical principle against it which seemed reasonable, it was in order either to show that it could be done or else why it could not be done.

Accordingly a 2-in. iron pipe 40 in. long was filled with the turnings which result as a waste product when the copper rolls used in the textile industry are turned down in a lathe. These turnings can be gathered in quantity and at a price below that of copper ingots. The copper used may contain considerable zinc and still be entirely suitable for the work. Four lbs. were tamped into the iron pipe to give a 28-in. column.

These pipes were heated in a combustion furnace to a low red heat and they easily gave 200 liters of nitrogen before they were exhausted. Then they were reduced with hydrogen and were again ready. I never used gasometers, but simply passed the air blast furnished by a small glass suction pump over the hot copper and then used the gas directly in the runs.

The arrangement is shown in Fig. 12 and shows how easily one can get the current of nitrogen automatically at constant pressure in any quantity varying from a few bubbles to 2 liters per minute. The tubes were run for months and were just as good as when they were first made.

It was then desired to construct a large commercial unit and in order to test how much sagging, analogous to that shown by the briquettes in Fig. 6, would take place, the horizontal pipe was, hence, purposely taken 12 in. in diameter by 10 ft. long and charged with the

copper turnings. It gave 300 liters of nitrogen per minute at first but in a few days was completely useless. Examination showed that the copper had sagged 4 in. and was, moreover, covered with iron scale from the pipe so that the air did not get in contact at all. In another case, about a 6-in. tube was placed vertically but the plastic copper soon compacted by its own weight so as to shut off the gas current.

These factors having been determined to be large, it was evident that they must be avoided. This was very easily done and the first furnace constructed did so well that I should simply duplicate it if more nitrogen were needed.

I used a vertical pipe 10 in. in diameter and 6 ft. long, which was heated in a furnace having two vertical flues, one for the burner flame and the other for the tube containing the copper. The supports for the copper were made from two ordinary 1-in. iron crosses with side openings which were connected by a threaded 6-in. piece of iron rod through the side openings. Then 4-in. iron nipples were turned into the 8 remaining openings so as to make the 8-armed support which would just slide down into the 10-in. pipe.

One was dropped in and the copper tamped down just level with the top of the cross with a stick. Then another support was dropped down so that it rested on top of the lower cross and copper was tamped in as before. This was continued until the top was reached and the pipe contained 280 lbs. of copper turnings. Every section of copper was thus supported firmly and independently. It could not sag from the sides because the tube was vertical. It could not compact itself because each section had to sustain only its own weight and whatever sag there was in a section could simply open a horizontal section which would do no harm.

This furnace was run hard for 6 weeks in the tests and I could not detect the slightest deterioration. It gave 16,000 liters of nitrogen in 2 to 3 hours before requiring reduction and then it was reduced by cautiously adding a number of liters of wood alcohol at the top. This served not only for reduction but also as a measure of the capacity of the furnace. I never heated it above 450° C. In actual practice one would reduce the copper with the carbon monoxide from the cyanizing furnace and on a large scale perhaps it might not be necessary to apply external heat since the reactions in the copper turnings are exothermic. The reductions should, hence, not be too energetic as otherwise it might heat the copper too high. I do not know how others construct their furnaces but this one is eminently satisfactory.

The expense of copper need hardly be considered because the cyanide produced would now pay for the copper every 40 minutes and even in normal times in less than half a day. If anyone is doing electrolytic work and has waste hydrogen, this will also give nitrogen with the utmost ease since it is only necessary to burn the hydrogen and air in regulated streams in a] very simple apparatus. It consists simply of

iron tubes which may be lined with fire-brick inside in the combustion space.

This is about the same as the above scheme with copper, only the copper is left out and the hydrogen and air act simultaneously. The steam formed condenses out and leaves the nitrogen which may contain a slight excess of hydrogen if desired and the heat generated can be used for evaporation purposes.

A still simpler device follows from my method of changing cyanide into urea as shown below. In fact, it will be seen that the nitrogen there becomes a waste product in nitrogen fixation and it may accumulate twice as fast as it is being fixed.

DISTILLATION OF CYANIDE

Having now shown methods of obtaining alkali cyanides, it is naturally in order to consider methods of getting the cyanide from the briquettes. One would wish to avoid lixiviation if possible and, hence, the following work on distillation. As we would destroy the catalytic solution surface by heating the iron-carbon mixture above the eutectic point (about $1120^{\circ}\text{C}.$) because of the iron melting to globules, it seemed worth while to try the distillation in either a current of nitrogen or in a vacuum. Both seem to work.

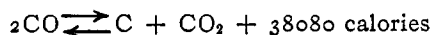
For example: Some cyanized briquettes were placed in a copper tube, heated to $1000^{\circ}\text{C}.$ and at about 2 mm. pressure. The cyanide collected in a pool which solidified to a clear mass which could not be told from glass by appearance. There was no cyanide whatever left in the iron-coke mixture and only the merest trace of alkali.

In another case the specimen of distilled cyanide was titrated and found to be 99.9 per cent NaCN. I have also distilled both sodium and potassium cyanides *in vacuo* while a melting point tube filled with sodium chloride was in the mixture. The sodium chloride did not melt; hence the cyanide must have distilled below this melting point (792 or $820^{\circ}\text{C}.$).

$\text{K}_2\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ were also heated *in vacuo*. This gave a fine distillate of KCN while iron-carbon in very finely divided form remained. This would be slightly wasteful but would work finely since the iron, carbon and nitrogen obtained in decomposition would go back into the cyanizing process again.

ASHLESS CARBON

The great promise of the above method of distilling cyanides would soon come to grief by having the ash from the coke accumulate with each repetition until it would stop the process. If we could get this carbon from carbon monoxide, it would be ideal. This suggests the following equation:



The equilibrium for this equation gives almost pure carbon monoxide at $1050^{\circ}\text{C}.$ while at $500^{\circ}\text{C}.$ it is almost reversed so that carbon monoxide must be unstable at low temperatures and if we could find a suitable catalyzer we should be able to get carbon from it.

I first passed pure carbon monoxide over ground coke but could notice no change. No carbon dioxide could be detected with the Hempel burette and only a trace of precipitate was obtained with lime-water. Evidently the catalysis was negligible.

The experiment was repeated as before in a combustion tube of hard glass which had a layer of finely divided iron in the bottom. A very striking change took place at once. The surface of the iron blackened at once and the issuing gas contained over 40 per cent of carbon dioxide in spite of the rapid current and the very slight contact. The catalysis must, hence, be exceedingly efficient and in a few hours the bulk of the whole charge had so increased from the deposited carbon that the entire section of the tube became filled so that the gas could no longer pass through.

The wonderful importance of this when applied to the iron-coke-soda ash can be seen at once. It gives us ashless carbon, in the form of very finely divided lampblack, together with 38,080 calories of heat developed within the charge itself. In addition, since the coke does not appreciably catalyze the reaction, the deposited carbon must, hence, be in very close contact with the iron.

We thus have this automatic process to do away with the ash in the carbon, with grinding the carbon, with mixing the carbon and iron and it provides internal heat in the briquettes themselves. It is, hence, equivalent to that much internal electric heating.

I will show how this will apply later under the theory of the continuous furnace. Suspecting that Mond¹ might have done such work in connection with his metal carbonyl compounds, I looked up the literature and found that he had done so. He found that with 15 parts of nickel, he could deposit 85 parts of carbon.

I also noticed that I could not obtain over about 43 to 45 per cent of carbon dioxide in the experiments and this suggests that there must be an equilibrium which should not be here if the process were one of pure catalysis since the catalyst should simply hasten the velocity of transformation but should not completely change its course.

A search of the literature revealed considerable work along this line from the point of view of the phase rule. Findlay² discusses the work of Baur and Glaessner, Boudouard and Hahn.

Fig. 13 shows a diagram embodying part of their important work on the equilibrium relation of carbon dioxide, carbon monoxide, iron and carbon at varying temperatures, while the dotted line in the curve shows what the relation should be if no catalyzer were present or if the catalyzer exerted no foreign function.

It is evident at a glance that as soon as the concentration of CO_2 reaches a certain value, it will begin to oxidize the iron to FeO , thus destroying the catalyzer and completely changing the action.

The curve *ABC* of Fig. 13 marks the concentrations

¹ *Jour. Am. Chem. Soc.*, 57 (1890), 749.

² Findlay, "The Phase Rule, 3rd Impression," page 306.

of CO and CO₂ which correspond to each temperature as long as any metallic iron is present. The maximum value we can get for the formation of CO₂ is hence about 42 per cent at the temperature of 680° C.

On the other hand, nickel does not form oxides as readily as iron and it will, hence, transform CO almost quantitatively into CO₂. This can be shown beautifully as a lecture experiment by placing finely divided nickel in a glass tube heated to perhaps 300 to 400° C. When pure CO is passed into the tube it is so completely transformed that the CO flame goes out and the exit gas contains 98 per cent of CO₂.

These phase rule studies are of great importance in the study of blast-furnace reactions, case-hardening, etc., and I will further apply them under the question of the oxidation of iron pipes.

OXIDATION OF IRON PIPES

In conducting the above process by external heating, the question of oxidation of iron pipes must be seriously considered, but, from some thousands of experiments I feel sure that this will not be of the slightest trouble when operations are based upon scientific principles. If we use electrical heating, the oxidation is absolutely avoided in the furnace shown above in Fig. 8, which was designed and built for this very purpose.

My experience leads me to believe that it can be entirely avoided in fuel-heated furnaces. For example, the temperature-concentration diagram in Fig. 13

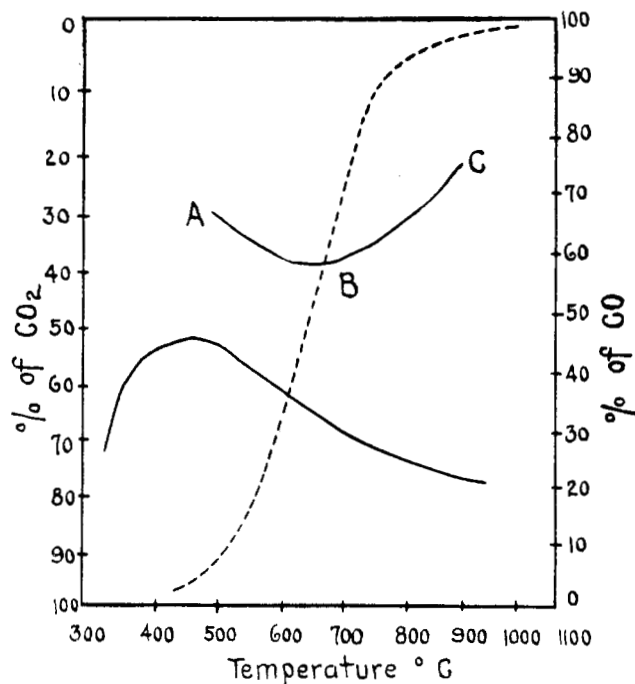
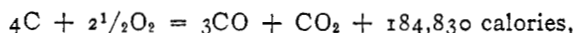


FIG. 13

shows that iron oxide cannot exist in the field above the curve ABC and, hence, it is impossible even to oxidize the iron pipe until the heating flame contains the corresponding value of CO₂.

For instance, if the iron pipe is heated to 950°,

then we could have 25 per cent of CO₂ present and still have oxidation impossible; that is, we could burn carbon according to the equation,



without any possibility of oxidizing the tube and then the remaining 203,010 calories could be obtained by admitting enough air in the preheating zone to burn the 3CO where oxidation would no longer take place because of the lower temperature. We might also combine the principle of the regenerative oven here if we desired.

These figures would be modified somewhat by considering the diluting influence of nitrogen, but I have only time to state general principles without giving details. It is very likely indeed that much more heat may be liberated in the heat zone because of the protective influence of a layer of oxide on the surface of the tube, but I always prefer to calculate on the most unfavorable case.

Also, we might consider admitting hydrogen with the producer gas as by having a steam-blown producer. The hydrogen present would then steadily diffuse through the red-hot iron walls as explained above under Fig. 1. The outward diffusing hydrogen, aided by the outward diffusing carbon and carbon monoxide, would meet the ingoing layer of oxide and would drive it back under the right conditions.

Also copper tubes would absolutely avoid this oxidation and they would easily stand the temperature. I have, in fact, used copper tubes largely at 950 to 1000° in another line of work with the greatest success. I could notice no damage to the tube either inside or outside. The expense of the copper would not be prohibitive and it could be cut down by using it only in the actual heat zone, and by using it as a sheathing for iron tubes; perhaps iron plated with copper would do. I have also tried nickel sheathing with results which would warrant a longer test.

There is no doubt that the trouble from the oxidation of iron tubes has been grossly exaggerated, and, personally, I feel convinced that there is nothing to it.

THEORY OF BATCH FURNACE

The theory of the batch furnace is also the theory of the process in its simplest form. We merely grind together intimately, iron, coke and soda ash, moisten and briquette the material. The dry briquettes are then heated in a vertical pipe, to say 950° C., in a current of nitrogen or producer gas until carbon monoxide no longer escapes. This is exceedingly simple and is all that there is to the process.

The theory is that the iron, by dissolving the carbon, gives a solid solution in which the carbon may move freely and it becomes active. This gives us our "catalytic solution surface."

It is hence only necessary to produce the extremely active catalytic solution surface, to maintain it unimpaired during the process, and to give the nitrogen and alkali metal or compound free access to the surface during the run.

ENRICHING PRODUCER GAS

You will note from Equation 8 that nitrogen gas is absorbed in the process and carbon monoxide is formed in large volume. The gas is enriched in a two-fold way and I have noted 75 per cent of carbon monoxide in the exit gas from the batch furnaces.

Bunsen and Playfair absorbed all their nitrogen; hence it is probable that under the right conditions producer gas can be enriched so that it will be substantially pure carbon monoxide.

DESTRUCTIVE EFFECT OF CARBON MONOXIDE

You will notice that in using producer gas, I always shut off the gas current before the briquettes began to cool. This is a vital point. For example, briquettes containing 19 per cent of sodium cyanide were heated red hot in a current of producer gas and cooled slowly

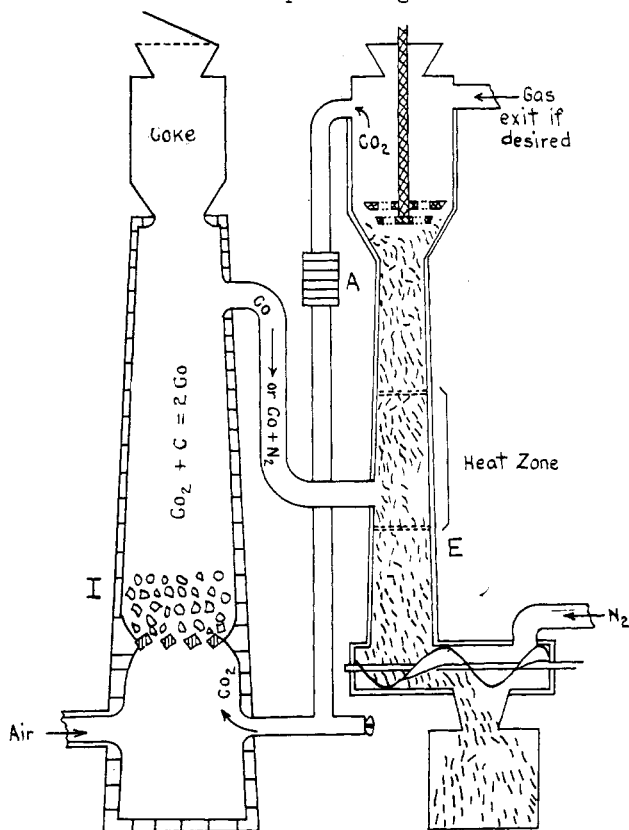


Fig. 14

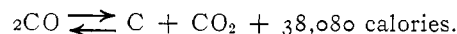
while the current continued. When cold, they contained only 3 per cent of cyanide of sodium. This shows that we have almost complete destruction of cyanide when the briquettes cool in a producer gas current and that we avoid all trouble in the above batch furnace, Fig. 8, by merely stopping the current before the charge cools, or, by dumping the hot briquettes so that the gas current can not pass through while they are cooling.

This destruction may well be due to carbon dioxide formed by the catalysis of the iron in causing the formation of ashless carbon by the equation $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$. If this be the true explanation, the iron acts both as a destructive and constructive catalyzer in the process.

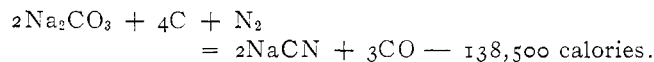
If this be so, then at 500 to 600° C., cyanide should be destroyed rapidly (see the temperature concentration diagram, Fig. 13) while, at, say, 950 to 1000° C., the CO_2 has almost disappeared and the speed of the cyanide formation has increased so that no harm is done. This is very important in the continuous furnace shown in Fig. 14.

THEORY OF THE CONTINUOUS FURNACE

It would take a separate paper to deal with the general features of such a furnace as that shown in Fig. 5. The briquettes passing in the top become preheated, by utilizing the waste heat from the gases of the reaction zone, and then collect all the cyanide fumes which are liable to distil in clouds from the batch furnace. When they get red hot they will, by catalysis of their iron content, produce the reaction



This gives finely divided ash-free carbon which is necessarily in intimate mixture with the finely divided iron. It also gives out heat in the briquettes themselves and therefore has the same exceedingly important effect as internal electric heating. Unfortunately the equilibrium relations of curve ABC in Fig. 13 must be applied, but, even if we take the maximum value at 680° C. this would contribute over 20,000 calories towards the 138,500 calories needed in the heat zone for the reaction



This is an exceedingly great advantage. Then in the cyanizing zone the same reaction takes place as in a batch furnace, but the intense volatilization from the porous briquettes carries the alkali upwards to be recondensed on the cooler briquettes above with corresponding heat changes. This distillation gives fine circulation of alkali to the solution surface and is carried back by the descending briquette column.

Below the cyanizing zone, the nitrogen cools the briquettes and itself becomes preheated so as to carry the waste heat back into the heat zone. The plastic briquettes now harden again and are removed by the conveyor. When producer gas washed with caustic alkali to remove CO_2 is used instead of nitrogen we have in some ways a very different problem.

For example, in a run in a 14 ft. 6-in. pipe which should have yielded at least 20 per cent of NaCN in the briquettes, I got only 5 per cent of cyanide when feeding at the rate of 2000 lbs. per day. When the feeding was reduced to 1000 lbs. per day the yield dropped to 1 per cent of NaCN in the briquettes. In view of the facts already disclosed it is evident that the producer gas destroyed $\frac{3}{4}$ of the cyanide formed with the 2,000-lb. feed, and when this was made slower the producer gas had a longer time to act and $\frac{19}{20}$ of the cyanide was destroyed.

This looked bad for the continuous process with the producer gas. The difficulty was overcome, however, by simply passing the producer gas into the briquette

column at the base of the heat zone. In this case the cyanized briquettes as they cool are entirely away from the current of producer gas (there must be no leak in the lower fitting of the furnace pipe, otherwise some of the producer gas would be forced downward with the briquettes and thus do harm).

This arrangement is shown diagrammatically in Fig. 14 and is arranged so that we may use either nitrogen or producer gas and it shows the principle of transferring carbon from one part of a closed system to another with oxides of carbon so as to separate from ash; incidentally such a simple modification in the furnace gives 25 per cent NaCN in the briquettes.

Even poor briquettes will give good results in these continuous furnaces. Some of the advantages can, however, be attained in batch furnaces by running the waste gases and fumes from the top of one into the bottom of the next furnace.

LIMITING FACTS

Suppose we consider, for example, a vertical 6-in. iron pipe, 6 ft. in length charged with briquettes of the usual size. Thus the speed of operation would be limited by the activity of the briquettes, by the rate at which nitrogen could be passed in, and by the rate at which heat could penetrate through the charge to the center of the core. Results already mentioned show that the briquettes are active enough to be cyanized in 1 or 2 minutes. The requisite nitrogen could be passed through them in 10 minutes. The heating could be done in 2 hrs. without undue excess of temperature outside.

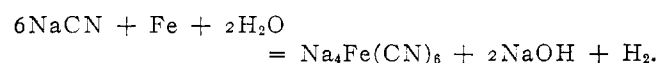
These data show why heat conduction is the slow factor and why internal heating by electricity or by the ashless carbon method are so interesting. Also the slow conduction determines the furnace design. It means above all else a long heat zone, just as long as possible, so that it will not be necessary to force an excessive amount of heat through a short heat zone with all the ruinous effects that follow.

I should use the full length commercial pipes of 20- to 24-ft. length unless the plastic briquettes compacted too much. In that case I should try slanting the pipes and if this did not work I would cut the pipe so as to bring the preheating zone in at an angle which should be sure to relieve the pressure.

SODIUM FERROCYANIDE

Having now shown how to fix nitrogen in the briquettes, it is in order to show how compounds can be recovered from them. If we add hot water to the cyanized briquettes to make a stiff paste and then steam them in an agitator you will see at once that we have an electrolyte of sodium cyanide and innumerable carbon-iron elements in contact with it.

We might hence expect to get as a result of electrical action, or otherwise, the following reaction:



This reaction takes place with great ease, hydrogen being given off in large quantity. After agitating for several hours, the hot mass is filtered and the black powder turned back into the process again.

The hot filtrate deposits an exceptionally fine quality of sodium ferrocyanide on cooling, and upon concentrating the filtrate the rest deposits out from the strong solution of caustic soda which is formed. The caustic soda is either turned right back into the process or used otherwise. The method is exceedingly effective.

LIXIVIATION FOR CYANIDES

From this behavior of the briquettes with hot water, we see that it will be necessary to observe certain precautions in lixiviating to get sodium cyanide. On the other hand, the solubility curve in Fig. 15 shows that at temperatures below 35° C. the mass will take up water of crystallization to form NaCN·2H₂O which will "set" the mass just like plaster of Paris.

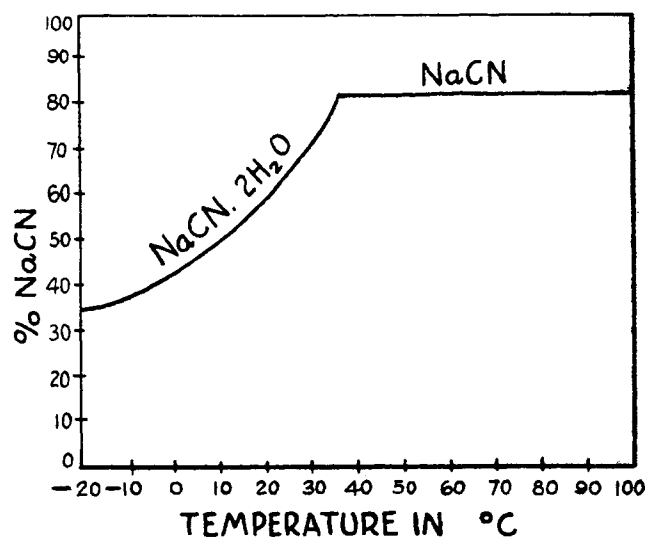
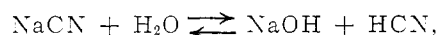


FIG. 15

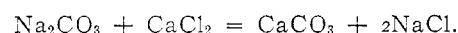
To avoid both dilemmas we should lixivate at a temperature slightly above 35° C., the transition point of the cyanide. This should be done quickly because the ferrocyanide reaction is going on slowly even at this temperature.

The solution can be concentrated *in vacuo* if desired. The cyanide is pure enough for many purposes. Or, it can be distilled as mentioned above. I have sometimes added lime to it to causticize any soda ash present as this would prevent the hydrolytic dissociation to form hydrocyanic acid,



for which manufacturers frequently add caustic soda intentionally.

Also we may add calcium chloride to remove the carbonate and replace it by sodium chloride thus:

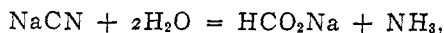


On then evaporating, we have the mixture of sodium

chloride and sodium cyanide which is so much sought in the jewelry trade.

AMMONIA AND SODIUM FORMATE

If we boil sodium cyanide solution to get ammonia and sodium formate,



we can only get to the boiling point of the solution. the action is slow and hydrocyanic acid is likely to form according to the already mentioned hydrolytic dissociation.

If, however, we add caustic soda (or prepare it with lime in the lixiviated solution), we get these effects: the caustic soda prevents hydrolytic dissociation to form hydrocyanic acid, it raises the boiling-point of the solution and it salts out the sodium formate from the solution by making it many times less soluble than in pure water.

The operation is carried out with a return condenser and the ammonia after passing through a caustic soda dryer is chemically pure and anhydrous and can be compressed at once into cylinders, if desired. The sodium formate can be turned back into the cyanizing process or it can be converted into sodium oxalate at once by merely heating *in vacuo*; from these we can easily obtain formic and oxalic acids.

UREA, AMMONIA AND NITROGEN

If we can arrange a flanged cast-iron pot, 3 in. in diameter by 12 in. deep, with a cover, inlet and

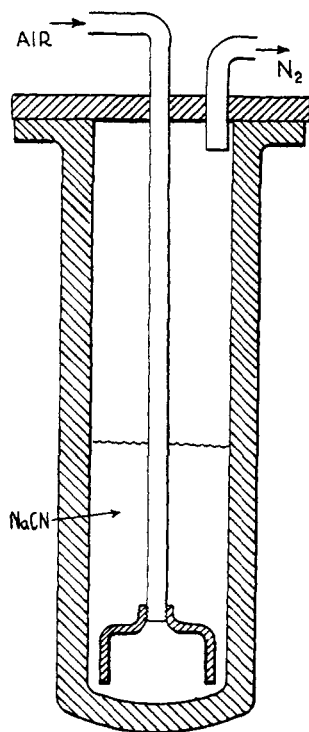


FIG. 16

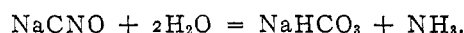
exit pipes, and a 2-in. reducing coupling as shown in Fig. 16, we have a serviceable laboratory unit to convert

cyanide into urea. The cyanide is kept just above its melting point and a current of air is passed through the molten cyanide. It burns to sodium cyanate according to the approximate equation,



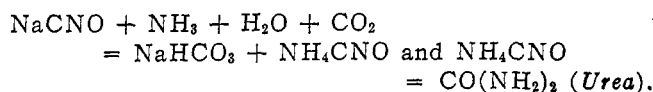
The nitrogen thus formed is turned into the cyanizing furnaces and this gives us 4 atoms of nitrogen for each 2 atoms fixed. The process hence takes its own nitrogen from the air to such an extent that theoretically one-half would have to be thrown away as a waste product in spite of the process being one for the fixation of nitrogen.

One-half of the cyanate is now heated with water which converts it into ammonia long before the boiling point is reached according to the equation,

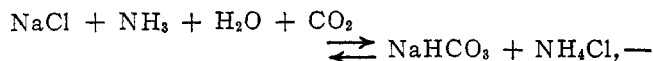


The sodium bicarbonate is thrown back into the process and the ammonia saved or else converted into urea as follows.

The other half of the NaCNO is added to water and the ammonia then passed in. Then CO₂ from the cyanizing furnaces is also passed into the liquid. The change is represented by,



You will notice that this is exactly similar to the ammonia-soda process,



the radical —CNO taking the place of the chlorine atom of sodium chloride.

The urea reaction takes place much better than the ammonia-soda one because the NH₄CNO is passed into urea and hence practically does away with reversibility while the NH₄Cl in the ammonia-soda process causes a loss of 30 or 40 per cent because of this factor.

The bicarbonate is returned to the process. We thus have a very inexpensive way of getting urea which has over 46 per cent of nitrogen and which is about three times as rich in nitrogen as sodium nitrate. It is about twice as rich in nitrogen as ammonium sulfate and would not introduce sulfuric acid into our soils, many of which are already too acid.

The urea was tested in water culture in the botanical laboratory of this university and found to give results equal to that of the nitrogen from potassium nitrate.

The urea may also be combined with nitric acid produced from ammonia so as to form urea nitrate (CO(NH₂)₂.HNO₃, which is still very rich in nitrogen but less soluble than urea.

METALLIC SODIUM

Sodium cyanide melts at a much lower temperature than salt and requires much less voltage for electrol-

ysis. My experiments indicate that it can be easily electrolyzed [$2\text{NaCN} = 2\text{Na} + (\text{CN})_2$] to sodium and cyanogen. This should give us a very cheap way of getting sodium from sodium carbonate with the incidental fixation of nitrogen.

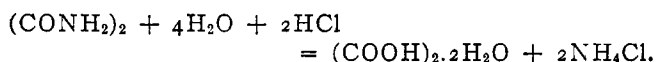
OXAMID, OXALIC AND FORMIC ACIDS

The cyanogen obtained from above was not supposed to be readily convertible into oxamid but I find it converts with the utmost ease under the right conditions. The gas is rapidly absorbed in hydrochloric acid (44 per cent) and then changes to oxamid thus: $(\text{CN})_2 + 2\text{H}_2\text{O} = \text{CO}(\text{NH}_2)_2$, which being practically insoluble separates out as a pure white powder.

Here we have the remarkable case of the hydrochloric acid acting as a catalyzer to concentrate itself even to the point of becoming gaseous, while at the same time precipitating out the resultant compound.

Curiously enough, the reaction practically stops when the hydrochloric acid is slightly dilute (14 per cent). The oxamid has nearly 32 per cent of nitrogen and is nearly insoluble in water and it should be especially of value as a fertilizer and should partially approximate the effect of the nitrogen in dried blood rather than that from the more soluble sodium nitrate. This has apparently already been verified by Dr. Hartwell of the Rhode Island Agricultural Experiment Station.

We get chemically pure oxalic acid from the oxamid by merely heating it for a minute or so with the concentrated hydrochloric acid to add more water, thus:



The acid crystallizes out free from all mineral salts.

The acid upon heating with glycerin transforms at once into formic acid according to the equation,
 $(\text{COOH})_2 = \text{HCO}_2\text{H} + \text{CO}_2.$

CAUSES OF FAILURE

A few of the large number of reasons for the absolute failure to achieve commercial results worthy of consideration by the methods described in this paper may be given:

(1) The omission of iron (which, by the way, is probably the only technically suitable catalyzer where alkali carbonates are used), absolutely ruins the process.

(2) Failure to mix the constituent properly is nearly equally ruinous and has no doubt contributed largely to failure.

(3) Heating a briquette a little too high will melt the iron at the eutectic point into globules, thus destroying the extended catalytic solution surface and thereby completely ruining the process.

(4) It is also above shown that simply putting a large vertical retort in the furnace horizontally will

completely ruin the process whenever the charge is plastic.

Alder preferred to mix his powdered materials with water and then with pieces of charcoal from "size of pea to size of fist." You can see at once that here the charcoal would absorb the molten cyanide just as a sponge absorbs water, thereby preventing the alkali from contacting freely with the catalytic solution surface even when he had one present by using iron. To show how serious this is, I prepared an active iron-coke-soda ash mixture according to my specifications which yielded cyanide of 98 per cent purity. A portion was then mixed with water and charcoal and it now yielded cyanide of only 14 per cent purity. This shows conclusively that Alder's preferred directions will ruin even an initially active mixture. You can now see why I was careful to have the screens spaced in Fig. 11 to keep the coke and briquettes apart.

(5) The above work shows that cooling a cyanized charge containing iron in producer gas ruins the process.

(6) Evidently oxygen would be worse and you can form your own inference about cooling the descending charge in nitrogen containing 2.5 per cent of oxygen.

(7) The quantitative measurement of heat penetration also shows that the heat zone should be long so as to allow time for the heat to penetrate to the center of the charge without having to force the process and thereby causing no end of needless trouble.

EMERGENCY PROCESS

I have carefully distinguished between what I have actually demonstrated with units which were of commercial size and those other things which have not been worked out as far.

In view of the conditions now existing, I wish to call attention to this topic so definitely that the issue will be so sharply defined that anyone interested can test the matter for himself by direct experiment within a few hours. This is a perfectly fair way of finding the truth or falsity of the statements and criticisms I have felt compelled to make.

If one wishes an operative process at once, it is only necessary to construct the furnace shown in Fig. 8. Construct a platform about 6 feet by 8 feet with 6 feet of free space underneath out of 4×6 timbers and 2-in. planks, cutting a hole through which the iron pipe may pass. Put on four small piles of brick to support the metal drum which should be, say, 30 in. in diameter by 6 feet in height and fill it with magnesia asbestos after inserting the drilled pipe and fastening with locknuts. Put on the reducing coupling, stuffing box and iron support as shown in Fig. 8 and drop in the brick support 8a and turn on the 8-in. receiving pipe.

This completes the furnace and with the help of several workmen, I would find no trouble in doing the whole thing in 6 hours. Briquettes are now added and

the copper leads attached. With sufficient current the first run will be finished and drawn within 2 hours and then runs can be made every hour; this can be kept up indefinitely if the drum be air-tight.

This furnace can be in operation in less than 24 hours, giving its output steadily and will easily yield 150 lbs. of sodium cyanide per 24 hours or over 200 lbs. of sodium ferrocyanide in the same time. An ordinary meat chopper will easily supply briquettes enough to run 8 such furnaces.

With over \$2.00 per lb. now asked for sodium cyanide, and with sodium ferrocyanide at over \$1.25 per lb. and potassium ferrocyanide at over \$7.00 per lb. within the past 10 months and great anxiety in both the mining and jewelry industries it seems that the above furnace which costs less than \$100.00 and can be put up and operating in less than a day might have been tried.

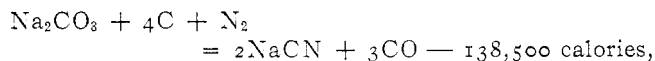
It would, at a stroke, either have shown how to relieve the situation immediately or else have shown that what I have been telling you to-night is worthless.

If no high amperage is available, the ordinary lighting current of 120 or 220 volts with iron rods analogous to the construction above indicated in Fig. 9 would work just as well. If electricity were not available then an oil burner would answer just as well as any burning-out of pipes would not need to be considered at such prices. I am not here advocating any particular furnace, hence there is no cause for discussion about its merit or lack of merit. It simply shows a means of getting away from endless discussion by doing something to get chemicals which are sorely needed.

These units could be enlarged and put in series to take practically any current and I have data for the design of a plant capable of producing the ammonia for 180,000 tons of nitric acid per year along these lines and it would be something which could be done quickly in case of need.

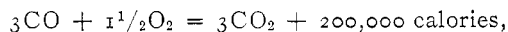
COST OF PROCESS

I do not have time to go into the question of cost of production this evening but I have estimated it very carefully from what I have actually tested with commercial units as well as from theory. I will hence say that the equation,

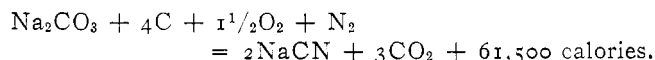


would theoretically require about 35,000 H. P. to produce 180,000 tons of nitric acid, allowing 85 per cent efficiency in oxidizing the ammonia.

But the three molecules of CO in the above equations would give on burning,



equivalent to about 50,000 H. P. to help make up the unavoidable heat losses. Combining these two equations we have



The total process is hence really an exothermic one and, in any case, it does not require electric power. Owing to its great simplicity and to the inexpensive materials, the cost is exceptionally favorable for the fixation of nitrogen and the production of cyanides, ammonia, urea and the other substances above mentioned.

COMPARISONS

We are now in a position to compare the above process with three of the commercial methods now in successful operation. The arc process which has been developed on such a large scale in Norway yields nitric acid and nitrates but it requires a very high temperature and is hence absolutely dependent not only on electric power, but, I think all agree that it can succeed only where the power is very cheap because the requirement of current is very large. It is further handicapped by yielding very dilute products which must be worked over.

The Cyanamid process requires calcium carbide which can be made practically only at the high temperatures of the electric arc. It is therefore also absolutely dependent upon electric power but it can make use of more expensive power than the arc process.

It has hence a correspondingly wider choice of locations. It is also handicapped by using nitrogen itself rather than producer gas.

My process differs from the above processes by operating at temperatures which may be below 950° C. and it is therefore independent of electric power. This means that it can be operated at any locality suitable for manufacturing purposes. I can use producer gas just as well as nitrogen and the process is therefore independent of pure atmospheric nitrogen. It is so exceedingly simple that it can be installed immediately with apparatus obtainable in the open market and because of the remarkable transformations of the cyanogen it opens the way for the cheap production of organic substances such as urea, oxamid, etc., as well as new commercial methods for oxalic and formic acids and many other substances I have in mind.

The Haber process fixes nitrogen by combining it with hydrogen and requires these substances in the pure state. It requires costly machinery, and its development required the highest type of engineering skill. These highly specialized things, however, mean that it will also require especially competent people to run it.

On the other hand, the process I have described to you this evening represents the other extreme. It makes use of the crudest things such as coke, producer gas and water. These are handled by the simplest possible mechanical operations and the catalyzer, iron, is not bothered even by the gross assortment of elements in the ash of the coke, and any sort of labor, when properly directed, can handle it.

REMARKS

It is not worth while to make a summary of the work I have described, because the whole presentation has been condensed so as practically to be a summary. Almost everything mentioned can be done in a variety of ways which I did not have time to mention and even the most important things could not be much more than mentioned.

I hope that the evidence presented to-night has cleared away some of the erroneous statements which have hindered progress in this field which has been handled in an exceptionally unfortunate way. I also hope that the statements under "Emergency Process" will, if sudden need arise, lead to instant action instead of interminable discussion and counter-propositions. The way to test the matter is to set up the apparatus as is sharply set forth. A roof can be put over it after it is in operation and blueprints, plans and improvements can await their turn.

None of the things mentioned in the above work were discovered by chance. All were predicted by a carefully considered application of the very simple but fundamental principles of physics, chemistry and mathematics, which every undergraduate in chemistry is taught. They were then verified by experiments which were chosen to give decisive answers to questions and to establish quantitative data.

Only a comparatively short time could be given to the work because of the heavy pressure of other duties, and it would certainly have been impossible to carry it out if it were not true that pure science is the only foundation for industrial work.

I have been connected with universities and technical schools for 28 years as student and teacher. I have always used every effort to further the view that all industries must be based directly on work in pure science and that the only way to succeed is to become thoroughly master of these fundamental principles and then look at things from every point of view in order to solve whatever problems may be encountered.

There seems to be a constantly increasing pressure both from within as well as from without the university, which is inimical to this ideal and many cures, which are at variance with it, are advocated, in the rush to get results quickly by a short cut to knowledge.

If it had been more generally realized that hard work and careful, self-sacrificing preparation are very likely ultimately to lead to quick, certain, solution of difficulties rather than perhaps to years of misguided effort and enormous expenditures of money, with, like as not, ultimate failure, things would not have drifted to their present condition.

If these illustrations have some influence in this direction I believe that it will be more important to the country than even a successful nitrogen fixation process.

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THE VOLATILIZATION OF POTASH FROM CEMENT MATERIALS¹

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In the course of an extended series of investigations upon the subject of potash volatilization from silicate mixtures, the following report was prepared, covering that portion of the laboratory work which was incident to the study of volatilization of potash from cement making materials.

The work reviewed in this report forms one link in a chain of investigations covering various possibilities of volatilizing potash from silicates during the process of manufacturing Portland cement, with subsequent collection of the volatilized potash from the furnace gases by means of electrical precipitation. The process of electrical precipitation can be applied in two ways: should the total dust and fume issuing from the furnace contain a large percentage of potash, the total suspended material can be collected in a single electrical precipitator; should, on the other hand, the potash content be low, a fractionation of the suspended material may be resorted to, as for example by utilizing a two-stage fractional precipitation apparatus.

OBJECT—It has long been known that the raw material used in cement making contains potassium salts which are partly volatilized in the burning, and from experiments in field and laboratory, some data bearing on this volatilization have been obtained and published. Very little exact information, and particularly such directly applicable to the potash volatilization from actual cement materials has, however, been available, and the following series of experiments were undertaken for the purpose of obtaining such information regarding the factors which influence the liberation of potash in actual cement burning.

SCOPE OF THE INVESTIGATION—The rate of volatilization of a potash salt from cement mix in the highly heated zone of a cement kiln, is dependent upon a number of factors. As predominating factors affecting the possible recovery in the furnace gases beyond the furnace, there may be mentioned: (1) the temperature prevailing in the kiln; (2) volume of gas passing; (3) the intimacy of contact between the furnace gases and the cement mix; (4) the vapor pressure of the potash salt or salts formed; (5) the possibility of dissociation under certain furnace conditions (oxidizing, neutral or reducing atmosphere or changing temperature) to components of greater or less volatility than the original salt; (6) the degree of saturation of the gas in contact with cement material; (7) the rate of diffusion both of the salt vaporizing in the interstices of the cement mix to the surface of contact with the gas stream, and of the saturated gas at the surface to the leaner gas areas beyond.

Furthermore, since in cement burning, cement material changes from a mixture of lime and clay to a clinker consisting largely of silicates and aluminates of calcium, the release or formation of the potash salt

¹ Report on Laboratory Investigation by the Western Precipitation Company.