

The Fixation of Nitrogen as Cyanide¹

By Richard Franchot

FERRO CHEMICALS, INC., WASHINGTON, D. C.

When working at a capacity of 40 million tons of pig iron, the American blast furnace is fixing nitrogen probably at the rate of 6 million tons a year and spending coke in doing it. This is double the rate at which it has been estimated that nitrogen is taken from our soil in crops. In terms of energy, the hearth of the blast furnace in the United States develops some 12 million kilowatts, of which

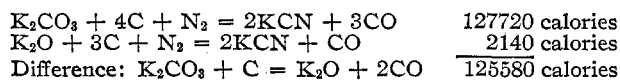
25 per cent is apparently available for and absorbed in work done at 1500° C. Of this it appears that one-half is devoted to keeping in circulation as cyanide a large accumulation of alkali. There appears to be power here of the order of 2 million horsepower, not only developed and available, but actually already engaged in nitrogen fixation.

IN THE process of the solution by chemical science of the problem involved in the return to the soil of an adequate proportion of the nitrogen removed by crops (the "nitrogen cycle"), certain inherent possibilities as to low cost in the fixation of atmospheric nitrogen as cyanide appear to have been as yet somewhat neglected. In view of these possibilities, the difficulties thus far encountered would seem to be well worth surmounting; and it may be said that these difficulties do not appear to be insurmountable.

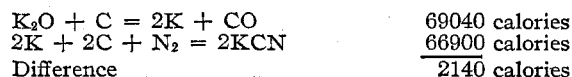
Since the discovery, about 1840, that alkali and carbon heated with nitrogen form cyanide, many attempts have been made to utilize the reaction for the commercial production of alkali cyanides. From Possoz and Boissiere^{1,*} in 1847 to Bucher² in 1917 the primary difficulty has proved to be that inherent in trying to deliver heat to the reacting materials at an adequate rate through the medium of externally heated retorts, the reaction being highly endothermic and absorbing great quantities of heat while requiring high temperatures for adequate speed. A secondary difficulty has been the loss of alkali by volatilization. Processes that involve heating by electrical means with removal of cyanide as vapor from the formation zone would not seem to be subject to these difficulties; but there is still another difficulty in that condensation with separation of the cyanide from by-product gases presents a problem of preventing the reversion of cyanide to alkali, carbon, and nitrogen which takes place in the presence of carbon monoxide at temperatures ranging below those at which cyanide formation occurs. In view of the comparatively high cost of electrical heating, the most promising method of commercializing the cyanide reaction appears to be that comprising broadly the use of mixtures of nitrogen and oxygen such as air, coupling the exothermic oxidation of carbon with the endothermic formation of cyanide. Certain patents lately issued to McElroy³ describe processes involving the application of this principle. The promise of the method is reinforced by repeated observation of the presence of cyanides in the blast furnace, where air or producer gas contacts with carbon and accumulated alkali at temperatures ranging up to 1500° C.^{4,5}

CHEMISTRY OF CYANIDE FORMATION

Typical reactions in which cyanide is formed from alkali may be written:

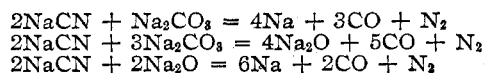


The chief endothermic component of the process of cyanide formation from carbonate is thus seen to be the reduction of carbonate to oxide, the further reduction to metal absorbing but little more heat than that set free in the formation of cyanide from its elements:



(The heats of formation are those given in Richards, "Metallurgical Calculations.")

In the course of an investigation of the cyanide reaction in the McElroy laboratory, it has been found that cyanide and carbonate react at about 1000° C. with evolution of alkali metal vapor. Upon heating a molten mixture of sodium carbonate and sodium cyanide in a retort, the effluent gases carry off relatively large quantities of metallic sodium as vapor. With an excess of carbonate the cyanide is completely decomposed, and with an excess of cyanide carbonate entirely disappears. So far as can be seen from the literature, this reaction has not heretofore been mentioned or described. The mechanism may include:



In the production of cyanide from alkali, carbon, and nitrogen, the carbon and nitrogen being in excess, cyanide itself may be made to play an important role as accelerator of the reduction of alkali and hence of cyanide formation, alkali metal formed by interaction of cyanide and alkali reacting exothermically with the excess of carbon and nitrogen to re-form cyanide with heavy increase. Systems comprising cyanide, alkali, carbon, nitrogen, and carbon monoxide come to equilibrium involving the relative concentrations of nitrogen and carbon monoxide, the temperature, and the ratio of cyanide to alkali. This equilibrium has been studied experimentally by feeding alkalinized charcoal more or less continuously into an electrically heated, vertical tube through which a current of nitrogen, producer gas, or air was passed. At three different temperatures the percentages of cyanide in the total alkali were found to be as follows:

Temperature ° C.	Nitrogen Per cent	CO + 2N ₂ Per cent	Air Per cent
950	96	40	38
1000	98	62	61
1050	98	93	94

The samples were taken from a point in the tube far enough from the gas inlet to insure that the material analyzed represented that which had been subjected to the noted temperatures and the stated gases for a time adequate to bring about equilibrium under the indicated conditions. Perhaps the most interesting of these results is the close agreement between the cyanide ratios for air and for producer gas. Essentially, the experiments show the result of heating alkali, carbon, and nitrogen in the presence of cyanide itself. The pronounced effect of temperature increase may be noted. These results are in fair agreement with those of Ferguson and Manning,⁶ and also with those of Ingold and Wilson.⁷ The figures indicate that at very slightly higher temperatures

¹ Received May 17, 1923.

* Numbers in text refer to bibliography at end of article.

cyanide is entirely stable in the presence of carbon monoxide and nitrogen in relative concentrations approaching those of producer gas. The figures suggest, too, that not far above 1050° C. a critical temperature is reached at which the velocity of cyanide formation from alkali is great enough to become a direct linear function of the rate of heat supply. In this connection the vapor pressure of cyanide is pertinent, since in this temperature range cyanide becomes volatile and since in a process of producing cyanide in the vapor phase the vaporization heat becomes a factor to be taken into account.

VAPOR PRESSURES OF SODIUM CYANIDE ⁸	
Temperature ° C.	Pressure Mm. of Mercury
1000	12.5
1050	21.4
1100	37.0
1200	90.0
1300	220.0
1350	300.0
1500	760.0

THERMODYNAMICS OF CYANIDE PRODUCTION

From the practical standpoint, the production of cyanide in any case depends upon a quantity supply of heat which must be available at cyanide-forming temperatures—that is, the temperature must be maintained against the cooling effect of cyanide formation—and in order to do this, available heat must be delivered to the reaction zone at a rate correlated with that of cyanide formation. In coupling cyanide production with the combustion of carbon with air oxygen, the heat development is limited to that of carbon monoxide formation, constituting only 30 per cent of the total combustion value of the carbon burned, 29,160 calories per mol. If recuperative principles are applied, a good proportion of this heat may be available for cyanide formation. For example, in a blast furnace (theoretical combustion temperature above 2000° C.⁹) the hearth temperature being usually about 1500° C., the heat quantity available at this temperature is about 1000 pound-calories per pound of carbon burned with air at a usual blast heat, the carbon being preheated during its descent through the shaft, thus:

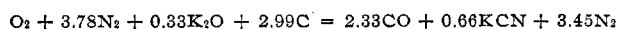
	Calories
Carbon monoxide formation from 1 pound carbon	2430
1 pound carbon at 1500° C.	654
5.6 pounds air at 600° C.	840
	3924
6.6 pounds carbon monoxide and nitrogen at 1500° C.	2700
Decomposition of blast moisture—5 grains per cu. ft. = 0.05 pound	160
Heat available at 1500° C.	2860
	1064

The available heat may thus be taken as 12,760 calories per mol carbon. At 1500° C., under usual pressures, cyanide is in the vapor phase, and to 63,860 calories, the heat absorbed in formation, must be added the heat of vaporization, 37,000 calories;⁸ the total heat absorbed in forming cyanide vapor from carbonate is thus 100,860 calories per mol potassium cyanide. This amount of heat comprises 62,790 calories for the reduction of carbonate to oxide and 38,070 calories for conversion of liquid oxide to cyanide vapor, these two components being in a ratio of 62:38 or 1:0.61. The heat available per mol carbon is equal to that absorbed in the formation from oxide of 0.33 mol cyanide vapor, or in the fixation as 1.78 pounds potassium cyanide vapor of 0.37 pound nitrogen per pound carbon burning with air; and the heat so becoming latent, if set free in condensation of cyanide and its reversion to oxide, is equal to the heat required to reduce carbonate to oxide equivalent to 61 per cent of the cyanide vapor so reverting. Hence, with alkali in the furnace, for example, if about two-thirds of the cyanide vapor-laden gases produced in the hearth are caused to pass up through the shaft and one-third are withdrawn from the furnace through outlet provided in the hot zone, the latent heat of the cyanide vapor carried into the shaft becomes available for the reduction of carbonate equivalent to the cyanide with-

drawn in the hot gas. Such amount of carbonate may be charged with the fuel at the top and descend toward the hearth in countercurrent to the ascending gases. Reacting with cyanide vapor, the alkali may be largely converted to cyanide before reaching the hearth. The output of cyanide from the furnace could thus be one-third of that cyclically formed, or the equivalent of 0.12 pound nitrogen per pound carbon burning with air. Moreover, if the fraction of hot gas withdrawn from the furnace is passed through a mass of alkalinized charcoal, the gas in cooling to about 1100° C. develops in cyanide condensation an amount of heat equal to that absorbed in the formation of a 50 per cent increment of liquid cyanide. The indicated ratio of nitrogen fixed is 18 per cent of the carbon burned with air, or about 4 per cent of the air nitrogen. In a modern blast furnace taking 40,000 cubic feet of air per minute and thus burning to carbon monoxide about 550 pounds carbon per minute, the availability of heat is such as to indicate a recovery of something like 100 pounds of fixed nitrogen per minute, or about 70 tons per day. The expenditure of not more than half the fuel value of about 7 pounds carbon at \$10.00 per ton would suggest an energy cost of less than 2 cents per pound nitrogen.

CYANIDES IN THE BLAST FURNACE—BEARING UPON FUEL ECONOMY

It appears that in the blast furnace are to be found the exact conditions under which, as indicated by the heat relations and by experimental observation, alkali is readily converted to cyanide with utilization of the heat of oxidation of carbon to supply heat absorbed in cyanide formation. There seems to be a rational basis for a nitrogen fixation process in which carbon is gasified by air and alkali in a reaction which may be pictured thus:



Under blast furnace conditions—that is, with carbon and alkali preheated and with air at 600° C.—the theoretical temperature of this reaction is 1500° C. With a higher blast heat, the proportions of carbon and alkali remaining unchanged, the reaction is exothermic at 1500° C. It will be noted that the reaction involves the fixation of over 8 per cent of air nitrogen as cyanide vapor in a concentration about 10 per cent by volume of the gases produced. The ratio of nitrogen to oxygen in the gases is 2.96:1.

That cyanide formation actually takes place in the blast furnace to a notable extent is a matter of repeated observation, the materials charged usually carrying an appreciable content of potash and soda. Moreover, there is to be found in the literature very strong evidence, amounting almost to conclusiveness, that through accumulation of alkali in the furnace cyanide vapor formation in the hearth of the blast furnace is generally of sufficient magnitude to constitute a most substantial heat absorbing factor. It is not too much to say that, although the bearing of cyanides in the furnace upon its fuel economy has not heretofore, so far as is known, been recognized, there are strong reasons for regarding cyanide vapor formation as a primary factor which accounts for the fact that the blast furnace functions very largely as a gas producer—the fact that the fuel energy is not over half developed, the equivalent of 70 per cent of the coke carbon burned leaving the furnace as carbon monoxide. It may be significant that this outstanding fact of practice has not as yet been otherwise adequately explained. The evidence that cyanides are of vital significance in the furnace economy may be summarized as follows:

The classic work of Bunsen⁴ showing substantial concentrations of alkali cyanides in gases taken from near the tuyeres.

The exhaustive study of Lowthian Bell¹⁰ on the circulation of cyanides in his furnaces, with observation of total alkali concen-

trations in the hearth gases as high as the equivalent of 0.02 pound potassium cyanide per cubic foot of gas, which is equal to 1.7 pounds potassium cyanide in 85 cubic feet of gas (under standard conditions) produced per pound of carbon gasified with air.

The very general statement in metallurgical textbooks that cyanides are found in notable quantities in the hot zone.

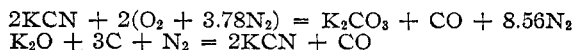
The phenomenon, accepted as fact and discussed by the older metallurgists, Percy, Lowthian Bell, Crooks, and others, that the ratio of the content of nitrogen to that of oxygen in the gases at the tuyere level is much smaller than the nitrogen ratio of the air as blown, and that the relative content of nitrogen becomes greater as the gases rise through a considerable height in the furnace. Lowthian Bell's analyses of the gases taken from one furnace at different times show the following ratios of nitrogen to oxygen (by weight).

	Air	At Tuyere Level	6 Feet above Tuyeres	11.5 Feet above Tuyeres
1	3.25	2.88	3.27	3.22
2	3.25	2.84	2.75	3.22
3	3.25	2.75	3.02	2.95
4	3.25	2.73	2.95	3.00
Average	3.25	2.80	2.99	3.10

Recent work by Perrott and Kinney, of the Bureau of Mines,¹¹ analyzing the gases which were sampled, by means of a tube inserted through the tuyeres, at different distances from the tuyere noses, the object being to investigate the speed of combustion. Following are the averages of the ratios of nitrogen to oxygen (by volume) calculated from the analytical figures on seven to ten different furnaces, the air ratio being 3.78 nitrogen per volume oxygen:

Distance from Tuyere Noses Inches	Volumes Nitrogen per Volume Oxygen	REMARKS
0	4.09	
4	4.34	
8	4.54	
12	4.23	11.2 per cent free oxygen
16	4.31	
20	4.38	
24	4.11	
28	4.00	
32	3.24	Free oxygen disappears
36	2.80	
40	2.87	
44	2.70	Carbon dioxide disappears
48	2.75	
54	2.66	
60	2.50	
66	2.17	
72	1.86	
78	1.91	
84	2.30	

These observations of Perrott and Kinney, being made on a straight line running from the tuyeres into the center of the hearth, are, as far as they go, in agreement with the generally observed decrease of the nitrogen-oxygen ratio in the gases formed at the tuyeres from that of the air. The variations are too great and too sharp to be explained by oxidation and reduction of the metal constituents. They are entirely in accord with what would be caused by successive decomposition and formation of cyanide in the reactions:



Cyanide formation takes nitrogen from the gases and puts oxygen into them; decomposition of cyanide adds nitrogen and subtracts oxygen. This explanation of the variation of ratio could be readily tested in individual furnaces by repeating Lowthian Bell's experiments, in which he found surprisingly large concentrations of cyanides and other alkali compounds, attributed to the accumulation by successive vaporization and condensation of exceedingly small proportions of alkali in the ore, coke, and limestone. The Bureau of Soils¹² has estimated an average of 0.2 per cent K_2O in the blast furnace materials used in the United States. This would indicate an input of alkali (potash and soda) to a 500-ton furnace of perhaps 5 tons daily. That the alkalies would accumulate to a concentration many times that due to the small quantity in the charge appears *a priori* probable, the usual basicity of slag tending to reduce its alkali content to a minimum.

Recently, the writer had occasion to measure the concentration of cyanide in gases issuing from the cinder notch of a

large furnace smelting Mesabi ores with a relatively low coke consumption. Analysis of the ore, coke, and limestone indicated an alkali input to the furnace equivalent to about 0.016 pound potassium oxide per pound carbon burning with air. This could cause a concentration of 0.00026 pound potassium cyanide vapor per cubic foot of gas formed at the tuyeres, 85 cubic feet per pound carbon. A number of measurements gave concordant results averaging 0.009 pound potassium cyanide equivalent per cubic foot of gas. This is a concentration thirty-four times that due to the alkali input. Such an average concentration in the hearth gases would involve 0.76 pound cyanide per pound carbon burning with air.

Relying upon the statements generally made in the literature that cyanides are usually present in substantial amount, it would appear that the generally observed variations of the nitrogen-oxygen ratio in the gases of the hot zone may be concluded to be due to formation and decomposition of cyanide. If this conclusion is sound, then the variation of this ratio may be taken as measuring the cyanide concentration in the gases, and hence the extent of alkali accumulation in the furnace. On this hypothesis, Perrott and Kinney's gas analyses indicate that in American furnaces generally alkali accumulation and cyanide formation are of about the same relative order of magnitude as in Lowthian Bell's furnace, where the gas composition in the tuyere zone would be accounted for by a net fixation as cyanide in that zone of about 5 per cent of the air nitrogen, the gas carrying 1.04 pounds potassium cyanide vapor per pound of carbon burning with air or 0.012 pound per cubic foot. This is considerably less than the concentration of cyanide and carbonate observed by Bell in the gas at 12 inches from a tuyere. Perrott and Kinney's average gas composition at 8 inches from the tuyere noses in eight furnaces shows a change in relative nitrogen content from 3.78 in the air to 4.54 volumes per volume oxygen, with yet 11.2 per cent free oxygen in the gas and hence 53.5 per cent of unchanged air. This suggests a nitrogen ratio of 5.41 in 46.5 per cent of the gas. Such a change of ratio would be brought about if for each pound of carbon burning to carbon monoxide with air a minimum of 0.96 pound potassium cyanide or its equivalent is burned to potassium carbonate—that is, if the gas formed from air carries 0.011 pound potassium cyanide vapor per cubic foot. The entering air forms a flame of burning oxygen in an atmosphere of producer gas, the carbon dioxide thus formed serving as a carrier of air oxygen to the coke. The changing gas composition near the tuyeres indicates that carbo-nitrogen compounds also serve as oxygen carriers and that there is a most substantial concentration of such compounds as vapors in the gases formed. At 32 inches from the tuyeres, where the free oxygen has disappeared, carbonate vapor has apparently again taken up nitrogen and given back its oxygen to the gases, while in addition the gas has lost nitrogen or gained oxygen sufficient to change the ratio to 3.24, a decrease of 14 per cent from the air ratio. Such a change is in concordance with Lowthian Bell's observations and would seem to measure a net formation from oxide of about a pound of cyanide vapor per pound of carbon burning with air.

The formation or vaporization of such a quantity of cyanide in the hearth of the furnace absorbs more than half of the heat available in the hearth with the usual blast heat and accounts quantitatively for the fact that the furnace burns about twice as much coke to carbon monoxide with air as is needed to give the heat absorbed in the smelting process proper. This excess heat may be held responsible for the low carbon dioxide ratio. Analysis of the furnace conditions leads to the conclusion that a withdrawal of gas from the hot zone and, correlated therewith, an addition of alkali to the furnace charge will, without interfering with iron production but with positive

benefit to the furnace operation, make possible the fixation and recovery of over 1 per cent of the air nitrogen.

BIBLIOGRAPHY

- 1—Richardson and Watts, "Chemistry of Acids, Alkalies, and Salts," Vol. III.
- 2—Bucher, *J. Ind. Eng. Chem.*, **9**, 233 (1917); see also Brown, *Ibid.*, **11**, 1010 (1919); Bartell, *Ibid.*, **14**, 699 (1922).
- 3—McElroy, U. S. Patents 1,466,624; 1,466,625; 1,466,626; 1,466,627; 1,466,628 (August 28, 1923).

- 4—Bunsen and Playfair, *Brit. Assoc. Advancement Science Rep.*, **1845**.
- 5—Lowthian Bell, "Chemical Phenomena of Iron Smelting."
- 6—Ferguson and Manning, *J. Ind. Eng. Chem.*, **11**, 946 (1919).
- 7—Ingold and Wilson, *J. Chem. Soc. (London)*, **121**, 2278 (1922).
- 8—Ingold, *Ibid.*, **123**, 885T (1923).
- 9—Richards, "Metallurgical Calculations."
- 10—Bell, "Chemical Phenomena of Iron Smelting," Chapter XXXIV.
- 11—Perrott and Kinney, *Trans. Am. Inst. Mining Met. Eng.*, February, 1923.
- 12—Ross and Merz, *J. Ind. Eng. Chem.*, **14**, 302 (1922).

Analysis of Gypsum and Gypsum Products¹

By F. C. Welch

BUREAU OF STANDARDS, WASHINGTON, D. C.

CALCIUM sulfate occurs in the natural state in two common forms, as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and as natural anhydrite (CaSO_4). It is also found sometimes as a double salt in several compounds, such as syngenite ($\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) and polyhalite ($2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$). Gypsum has many uses, anhydrite very few. As some anhydrite is usually contained in the gypsum, a satisfactory method of determining quantitatively the amounts of each present is necessary.

In the gypsum industry, however, there are four well-defined crystalline forms in which calcium sulfate is found: (1) gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), (2) calcined gypsum or hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), (3) soluble anhydrite (CaSO_4), and (4) natural anhydrite (CaSO_4). Gypsum itself is used as land plaster and retarder in Portland cement. The hemihydrate, which is commonly called plaster of Paris, is made by calcining gypsum at about 140°C . This material is used in many ways, as wall plaster, molding plaster, etc. Soluble anhydrite, known as second settle stucco, is made by calcining gypsum at about 200°C ., but owing to its instability it must be used immediately after calcining. This product is sometimes used in making partition tile. Natural anhydrite takes up water very slowly to form gypsum and has very few uses at present. However, it is sometimes used as a filler in paints. A product similar to natural anhydrite may be prepared by heating gypsum at about 600°C . for several hours.²

These different forms may be distinguished microscopically,³ but no satisfactory method of chemical analysis has been developed that will determine how much of each form is present. The microscopic method, however, requires a knowledge of microscopic optical mineralogy which is not at the command of the ordinary chemist.

PRESENT METHOD OF ANALYSIS

The method in use at the present time for distinguishing the amounts of each constituent present is one recommended

Samples of raw gypsum were analyzed for gypsum and anhydrite according to present recommended method of analyses (Proc. Am. Soc. Testing Materials, 1921) and checked by microscopic analysis. The method was found to be unsatisfactory, variations of from 1 to 8 per cent occurring. The present method does not distinguish between the different forms that may be present: (1) gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), (2) calcined gypsum ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), (3) soluble anhydrite (CaSO_4), and (4) natural anhydrite (CaSO_4). The following method is recommended which enables the chemist to determine the percentages of these constituents present in their mixtures: If gypsum, determine hygroscopic moisture by drying sample in air having a vapor pressure slightly greater than dissociation pressure of gypsum; then determine total combined water by drying at 200°C . If calcined gypsum, determine the total combined water as for gypsum and then pass air dried by 25 N sulfuric acid over sample to constant weight. From the total combined water, water taken up by sample from 25 N sulfuric acid to form $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, and analysis for CaO and SO_3 , the amounts of gypsum, calcined gypsum, natural anhydrite, and soluble anhydrite may be calculated.

by the American Society for Testing Materials.⁴ It consists substantially in heating a thin layer of not less than 450 grams (about 1 pound) of the sample at 45°C . for 2 hours in order to drive off any hygroscopic moisture present (A. S. T. M. specifications for 1919 require that the hygroscopic moisture be driven off at 60°C .). One gram of the dried sample is then ground to pass a No. 100 sieve and heated in a covered crucible at 215° to 230°C . to constant weight in order to drive off the combined water. From the analysis of a sample for CaO, SO_3 , and combined water,

the amounts of gypsum and anhydrite are calculated.

The objections to this method are many:

1—From the vapor pressure curve of gypsum it will be seen that some of the combined water under some conditions would be driven off at either 45° or 60°C .⁵

2—Fine grinding of the gypsum is liable to cause serious error in the determination of combined water.⁶

3—The soluble anhydrite takes up water rapidly from air while being weighed in a crucible, and has a tendency to take up water from calcium chloride and sulfuric acid in a desiccator.

4—The results obtained do not show which constituents are present. For instance, in a mixture of gypsum, calcined gypsum, and natural anhydrite there is no way of telling in what combination the combined water is present, and accurate analyses are impossible.

SEARCH FOR IMPROVED METHOD

With these considerations in mind work was started on an improvement of the present method, or the development of a new method which would be accurate and would enable the chemist to distinguish between the four materials likely to be present. Samples of gypsum as fed to the calcining kettle were obtained from several manufacturers. These samples were screened and four different screenings obtained—on a No. 70, No. 70 to 100, No. 100 to 200, and past a No. 200 sieve. The amounts of gypsum and anhydrite present in each separated part and in the original sample were then

¹ *Proc. Am. Soc. Testing Materials*, **21**, 590 (1921).

² Received July 10, 1923. Published by permission of the Director, U. S. Bureau of Standards.

³ Stone, *Bur. Mines, Tech. Paper* **155** (1917).

⁴ *Proc. Am. Soc. Testing Materials*, **19**, Pt. 1, 617 (1919).

⁵ Calderon, *Bol. real. soc. esp. hist. nat.*, **11**, 756 (1911); *Z. Kryst. Mineralog.*, **54**, 200 (1914).

⁶ Steiger, *U. S. Geol. Survey, Bull.* **413**, 70 (1920); Hillebrand, *J. Am. Chem. Soc.*, **30**, 1120 (1908).