

in connection with the nitrogen content of the crop, and it is fair to infer from the data collected during the three seasons that the tendency of the vegetable soil rich in nitrogen is to increase the total nitrogen content of oats grown therein, but that this increase is chiefly due to the content of non-proteid nitrogen.

CONCLUSIONS.

(1.) Oats grown upon humus soils contain about twenty-five per cent. more nitrogen than those which are grown upon ordinary agricultural soils.

(2.) The increase in the amount of nitrogen noted above is found chiefly in the amid, and not in the proteid nitrogen.

(3.) Fertilization of humus soils, such as were used in these experiments with potash and nitrogenous fertilizers, did not have any appreciable effect upon the quantity of the crop.

(4.) The use of phosphatic fertilizers in connection with these humus soils greatly increases the quantity of the crop and diminishes the percentage of nitrogen contained therein. This diminution in the percentage of nitrogen appears to have resulted chiefly from the increase in the crop, and not to any deleterious influence of the phosphatic fertilizer.

(5.) The three forms of phosphatic fertilizer employed, *viz.*, finely ground soft Florida phosphate, phosphatic slag, and acid phosphate exert an almost identical influence in increasing the quantity of the crop.

(6.) Oats grown upon humus soils absorb directly therefrom a portion of the nitrogen contained therein, chiefly in the form of non-proteid nitrogen.

My thanks are due Mr. T. C. Trescot for his valuable assistance in the nitrogen determinations.

NOTES ON THE DETERMINATION OF INSOLUBLE PHOSPHORUS IN IRON ORES.¹

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ONLY within the past few years have chemists recognized the importance of the fact, that comparatively large amounts of phosphorus may occur in the siliceous residue left

¹ Read at the Chicago Meeting, 1897, of the A. I. M. E.

from the acid treatment of iron ores. We know of one case in which an ore contained about three times as much phosphorus in the insoluble as in the soluble form. It was disposed of at a premium, as an exceptionally high grade Bessemer ore containing 0.010 per cent. of soluble phosphorus, while the insoluble phosphorus brought the total amount up to 0.040 per cent.

The magnetite and the specular hematite of the Lake Superior districts, and the fine ores of the Mesabi range, as a rule, contain very small amounts of insoluble phosphorus. But the mining of the soft hematites and the progressive lowering of the phosphorus limit in a strictly Bessemer ore, have combined to make the determination of insoluble phosphorus one of the routine requirements in all analyses of Bessemer ores.

The insoluble phosphorus is understood to be that phosphorus which cannot be extracted by boiling hydrochloric acid of 1.10 specific gravity. The time given for the extraction of the soluble phosphorus will vary, of course, according to the nature of the ore. In ordinary practice the boiling is continued until the residue is white, or only very slightly tinged with ferric oxide. This ordinarily takes from half an hour to an hour. The prolonged boiling of ores known to contain considerable quantities of insoluble phosphorus has failed to extract any appreciable amount of additional phosphorus. Very fine grinding and subsequent sifting through bolting-cloth, has not increased the extraction. These statements represent the result of experiments carried out to test the opinions of a few chemists, who have maintained that such operations would materially increase the solubility of the phosphorus, generally supposed to be insoluble. The determination of this insoluble phosphorus in laboratories required to make a large number of analyses of ores daily, has added a considerable burden to the ordinary routine work.

The current practice in the treatment of the residue remaining from the acid solution of the ore, in order to transform the phosphorus into soluble form, is to fuse the siliceous residue with sodium carbonate in platinum crucibles, dissolve the fused mass in weak hydrochloric acid and evaporate to dryness to dehydrate the silica. The sodium phosphate is then extracted with weak hydrochloric acid and treated in the usual way for obtain-

ing the precipitate of ammonium phosphomolybdate. This operation requires considerable time and manipulation, and involves the introduction of sodium salts, which sometimes prove unfavorable to the obtaining of a pure precipitate of ammonium phosphomolybdate.

The practice of fusing the ore direct with sodium carbonate, and thus extracting the total phosphorus, requires larger platinum crucibles, and would not be practicable where so many determinations have to be carried on simultaneously, as in the case under consideration.

Hydrofluoric acid has been used to dissolve the insoluble residue, but care has to be taken to evaporate the excess of acid employed if the solution is to be subsequently placed in glass beakers.

Since there has been such increased demand for siliceous ores to mix with the low silica ores of the Mesabi range, chemists have been more than ever annoyed with the determination of insoluble phosphorus, as the increased amount of siliceous matter in the residue has required for fusion proportionately more sodium carbonate, heat, time, and patience.

For this reason we began a series of experiments with the purpose of finding a more rapid and convenient method of determining either the total phosphorus or the insoluble phosphorus by itself.

In the first experiment the ore was intimately mixed with less than an equal bulk of sodium carbonate, and then subjected to a red heat in a platinum crucible, the idea being to convert all the phosphorus into sodium phosphate, without using sufficient sodium carbonate to make a liquid fusion. The results were encouraging. The calcined mixture of ore and sodium carbonate are readily freed from the crucible and easily broken up by the pressure of a glass rod in the beaker. The mass was then boiled in some cases with water alone, and in other cases with weak acids, and the total phosphorus was quickly extracted from many ores containing considerable amounts of insoluble phosphorus. The main objection to this method was encountered, however, when the siliceous ores were treated by it. In such cases, owing to the large amount of siliceous residue, no matter how little sodium carbonate was used, it was difficult to prevent

a partial fusion, forming silicate of sodium, and thus making it hard to remove the calcined mass from the crucible.

Calcined magnesia was next tried as a base to combine with the insoluble phosphorus, and excellent results were obtained, no trouble being experienced with the fusion of the large silicious residues. It was, however, somewhat surprising that the magnesia acted so readily in extracting the phosphorus.

In the experiments next made the ore was calcined without the admixture of any base, and after this operation it was treated in the usual way with hydrochloric acid, when it was found that the total phosphorus had been extracted. This treatment was successful with most of the ores tried, but had the disadvantage of rendering the ferric oxide less readily soluble, and thus increasing the time required for the subsequent solution.

Applying this idea of simple ignition to the insoluble residues only, it was found that all the insoluble phosphorus could be thus converted into the soluble form, and a very simple practical method was thus established.

Very recently our attention has been called to the fact that Mr. Lychenheim¹ and Mr. Norris² had come to the same conclusion in the determination of phosphorus in coal and coke—namely, that fusion can be dispensed with and simple ignition substituted. Mr. Lychenheim has also informed the authors that he has found it to be perfectly satisfactory in the case of ores.

The details of our practice are as follows: About one and a half grams of ore are dissolved in a No. 3 beaker with twenty-five cc. of hydrochloric acid, 1.10 specific gravity. When the ore is dissolved, the excess of acid is evaporated until the solution begins to assume a syrupy consistency. It is then diluted with water and filtered into an Erlenmeyer flask, and the filter-paper and residue are placed in a platinum crucible and ignited. When the paper is burned off the residue is broken up with a platinum rod and ignited at a red heat for a couple of minutes, when it is removed and placed in a beaker for solution. Water is added, together with a few drops of hydrochloric or nitric acid, and the solution is brought to a gentle boil for about five minutes. It is then filtered into the flask containing the soluble

¹ A. I. M. E., 24, 66.

² *Ibid.*, 24, 362.

phosphorus (or into another flask, in case it is to be determined separately)¹, neutralized with ammonia, and precipitated as ammonium phosphomolybdate. The latter precipitate is titrated according to Handy's modification of the sodium hydroxide method.

This method having been found by many tests to give perfectly reliable results, has been in use in our laboratory for more than a year. The following table exhibits a few of the many analyses made by us to satisfy ourselves as to the accuracy of the method.

In order to obtain some general idea of the nature of the base, which was combined with the phosphorus in the insoluble form, we made the following partial analysis of the insoluble residue from the hydrochloric acid treatment.

After drying the residue at 100° C., it was subjected to ignition in a platinum crucible for five minutes :

	Per cent.
Loss on ignition.....	5.05
Loss due to extraction by acid*.....	16.25

The residue from the above treatment contained, in percentages of the original residue :

	Per cent.
SiO ₂	74.25
Al ₂ O ₃	2.70
CaO.....	1.37

TABLE OF PHOSPHORUS DETERMINATIONS.

Method A.—Solution of ore and fusion of residue with sodium carbonate (old standard method).

Method B.—Solution of ore and ignition of residue without flux (proposed method).

Method C.—Ignition of ore without flux, and subsequent solution, determining total phosphorus.

¹ It has been found that it is better to determine separately the soluble and insoluble phosphorus. Otherwise a too dilute solution is liable to be obtained for the precipitation.

	Name of ore.	Soluble phosphorus.	Insoluble phosphorus.	Total phosphorus.	Method.
1.	Wiuthrop ¹	0.051	0.008	0.059	A.
	"	0.051	0.008	0.059	B.
2.	"	0.039	0.008	0.047	A.
	"	0.039	0.008	0.047	B.
3.	"	0.054	0.014	0.068	A.
	"	0.052	0.015	0.067	B.
	"	0.067	C.
4.	"	0.051	0.008	0.059	A.
	"	0.058	C.
5.	Cambria	0.052	0.004	0.056	A.
	"	0.053	0.003	0.056	B.
6.	Lillie	0.065	0.006	0.071	A.
	"	0.065	0.007	0.072	B.
7.	Lake Superior.....	0.021	0.006	0.027	A.
	"	0.020	0.006	0.026	B.
8.	"	0.112	0.022	0.134	A.
	"	0.135	C.
9.	Salisbury	0.058	0.009	0.067	A.
	"	0.058	0.010	0.068	B.
10.	"	0.028	0.019	0.047	A.
	"	0.028	0.019	0.047	B.
11.	"	0.046	0.006	0.052	A.
	"	0.046	0.006	0.052	B.
12.	Cleveland Hematite.	0.022	0.015	0.037	A.
	" " .	0.022	0.016	0.038	B.
	" " .	0.021	0.016	0.037	B.
	" "	0.038	C.

The solution (marked *) from the ignited residue contained in percentages of the original residue :

	Per cent.
Al ₂ O ₃	9.55
CaO.....	0.92
B ₂ O ₃	4.10

From the latter analysis it would appear that the greater part, if not all, of the phosphorus was combined with the alumina.

The conversion of the insoluble phosphorus into the soluble form by simple ignition is a matter of some theoretical interest. The formation of a more soluble phosphate under such conditions certainly does not appear probable. Possibly the method proposed by Berzelius² for the decomposition of phosphates, by means of silica and sodium carbonate, may involve a reaction somewhat similar to that which we have here under consideration.

¹ Nos. 1, 2, 3, and 4 are silicious ores.

² Fresenius, 6th German edition, 1, 416.