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## THE MECHANICAL ANALYSIS OF BASIC PHOSPHATIC SLAGS.

By H. W. WILEY.

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BEFORE discussing the subject matter of the paper which I now present, I think it desirable to give a short sketch of the earlier literature relating to basic slags and the methods of their valuation.

In 1882, while examining some very finely ground bone in the Laboratory at Purdue University, Lafayette, Indiana, I noticed a marked solubility of the phosphoric acid therein in neutral citrate of ammonia. At that time Mr. H. A. Huston, who was a student in my laboratory, was directed to make some investigations of this phenomenon, and the results of his work were incorporated in his thesis for graduation, and the data were published in the proceedings of the Agricultural College of Indiana, Purdue University, for the year 1882.

In 1886 Jensch noticed that when lime and tricalcium phosphate were ignited together and the resulting mass pulverized, both citric acid and neutral ammonium citrate would extract phosphoric acid from the powder.<sup>1</sup>

In 1887, I published in *Agricultural Science* (March number) an article on the use of phosphorus contained in iron ores as a fertilizing material, after the conversion of the ores into iron or steel.

In 1889, I received from the Pottstown Steel Works a sample of phosphatic slag which was sent me under the name of cinder.

The superior merits of basic phosphatic slags as a fertilizer led me to believe that they might be largely soluble in neutral citrate solution. I therefore had this sample examined by Messrs. McElroy and Krug with that object in view. It was found to contain 20.20 per cent. total phosphoric acid, of which 12.25 per cent. were soluble in neutral ammonium citrate, the official solution used for the analysis of phosphatic fertilizers. An account of this property was published in the *Journal of Analytical Chemistry*, October, 1889. In this paper it is stated: "From the above results it is seen that in the phosphate slag we have a form of phosphoric acid equivalent in value to a first-class superphosphate."

<sup>1</sup> *Ber. d. chem. Ges.*, 19, 3093.

Petermann, in 1889, called attention to the fact that the calcium phosphatic limestone gives up phosphoric acid to a citrate solution.<sup>1</sup> In 1890 Jensch proposed the use of citric acid for the separation of tetra- from tri-calcium phosphate.<sup>2</sup> In 1892 Foerster published the statement that tetracalcium phosphate is easily soluble in ammonium citrate solution.<sup>3</sup>

Wagner proposed a special ammonium citrate solution having an excess of citric acid as a solvent for the tetracalcium phosphate in basic slags, and published an account of it in 1893.<sup>4</sup>

Since then the literature on this subject is very extensive, and it would be out of place here to attempt to cite the papers which have been published. It appears, from a study of the literature, that the first published account of the application of ammonium citrate as a method of valuing the availability of phosphatic slag was made from this laboratory in the paper published in the *Journal of Analytical Chemistry* above noted. For some reason, however, the method itself is universally known as the Wagner process.

Experience has shown that the official method of determining available phosphoric acid, applicable to the reverted phosphoric acid in superphosphates, is of varying value when applied to phosphatic slags. The composition of phosphatic slags has been previously described by Krug and myself.<sup>5</sup> It is evident that the tetrabasic lime phosphate is less stable than the tricalcium phosphate and hence the phosphoric acid which it contains is more readily given up to the growing plant. When a basic phosphatic slag is treated with neutral ammonium citrate in the regular official manner, the quantity of phosphoric acid which passes into solution is, as a rule, far less than the available content of phosphoric acid as indicated by the effect of the fertilizer upon a growing crop. For this reason other methods of determining available phosphoric acid have been proposed and the one now in use is known as the Wagner process in which a strongly acid ammonium citrate solution is used as a solvent.<sup>6</sup> The method of solution employed is a purely arbitrary one but gives results generally comparable to the effects produced in the field.

<sup>1</sup> *Chem. Centrbl.*, 1889, 2, 1036.

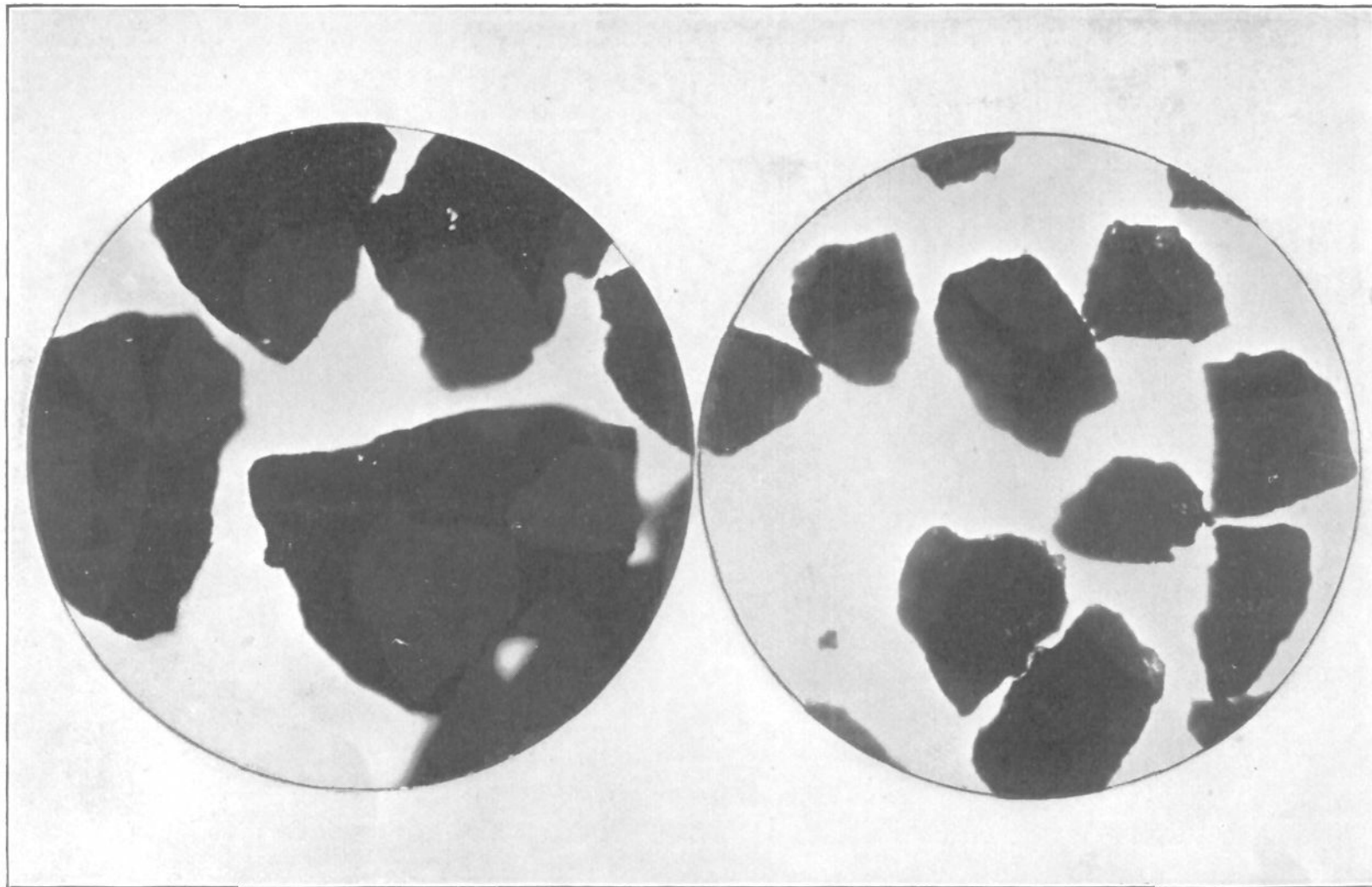
<sup>2</sup> *Ztschr. angew. Chem.*, 1890, p. 504.

<sup>3</sup> *Ztschr. angew. Chem.*, 1892, No. 113.

<sup>4</sup> *Chem. Ztg.*, 13, 1153.

<sup>5</sup> *J. Anal. Appl. Chem.*, 5, p. 685.

<sup>6</sup> Wiley's *Agricultural Analysis*, 2, 80.

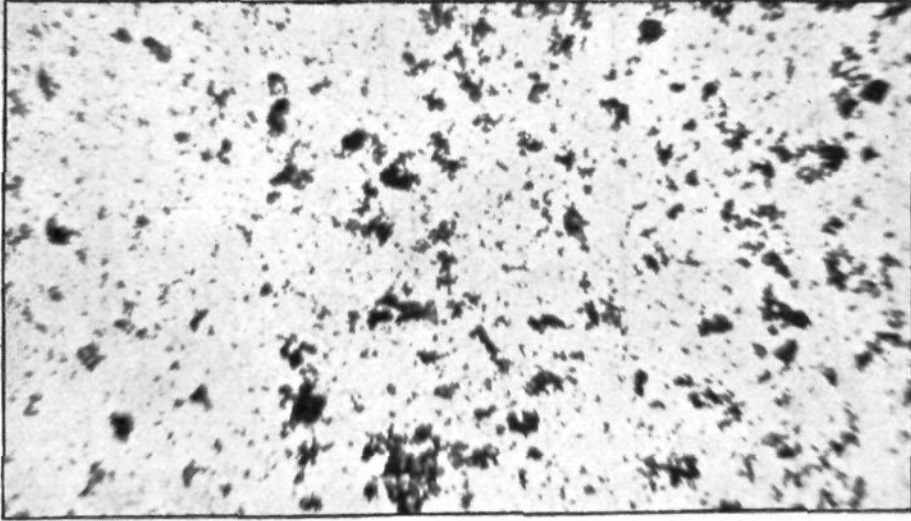


No. 1.     $\times 60$ .  
Greater than 0.25 millimeter in diameter.

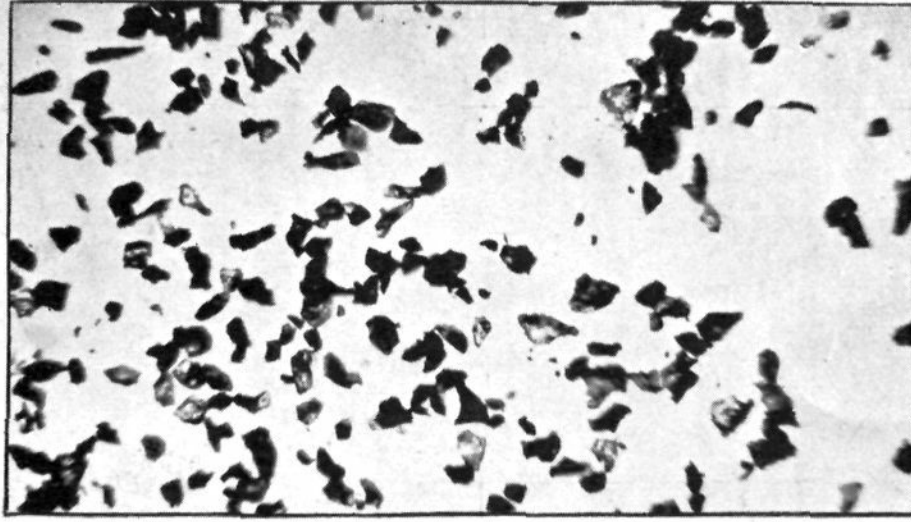
No. 2.     $\times 60$ .  
From 0.10 to 0.25 millimeter in diameter.



No. 3. X 60.  
Less than 0.10 millimeter in diameter.



No. 5. X 60.  
Remaining suspended in alcohol for five minutes.



No. 4. X 60.  
Remaining suspended in alcohol for two and one-half minutes.

The action of this solvent on phosphatic slags is very different for different samples. In some cases almost the whole of the sample is composed of pure tetracalcium phosphate and in these instances the solvent action of the reagent is very high. In other cases the sample may contain tricalcium phosphate, particles of silicious slags and also of iron and steel. In these instances, a low solvent action is noticed. It therefore has seemed desirable to supplement the chemical analysis of the slags with a mechanical separation. For particles of one-tenth of a millimeter in diameter and above, this separation is easily effected in a series of sieves, the finer sieves being made of bolting cloth. It is evident that a further separation of the fine particles cannot be secured with water, by reason of the action of this reagent upon the free lime which the slag contains.

About four years ago, I made some experiments looking to the substitution of alcohol in the place of water in the mechanical analysis of soils. The preliminary experiments succeeded so well that it was deemed advisable to use alcohol for securing the separation of the finer particles of the slag. The separations were made for me by Mr. C. C. Moore of the laboratory staff. The method of procedure is as follows: From twenty to fifty grams of the slag are placed in a shaking bottle and vigorously agitated for a few minutes on a milk-shake machine with ninety per cent. alcohol. This treatment serves to break up all the flocculates the sample may contain. The sample is placed in beakers entirely similar to those which are used in the mechanical separation of the soils by the subsidence method.

At first it was only desired to secure two series of separates of the fine particles and these were obtained by an arbitrary time of subsidence. All the particles which remained in suspension in a column of fifteen cm. of alcohol for five minutes were collected together and marked as separate No. 5. When all the particles which thus remained in suspension had been removed, another separation was made consisting of those particles remaining in suspension in like conditions, for two minutes and a half. This portion of the sample was collected and was designated as separate No. 4. The remaining portion of the sample was freed of alcohol and separated into three portions by sifting through two sieves made of bolting cloth with meshes of one-tenth and one-quarter of a millimeter diameter respect-

ively. All that portion passing through the one-tenth millimeter mesh is designated as separate No. 3. The portion passing the quarter millimeter mesh but not passing the tenth millimeter mesh is designated as separate No. 2. The portion not passing through the quarter millimeter mesh is designated as separate No. 1. The remarkably uniform size of these separates is shown by the accompanying photographs in which they are represented as magnified sixty diameters. By an inspection of separate No. 5, it is seen that it could be easily divided and another finer portion be secured, by means of a ten minutes subsidence in alcohol.

The alcohol used for the separation is of ninety per cent. strength.

The original sample and the separates were subjected to a chemical analysis, conducted for me by Mr. E. G. Runyan of the laboratory staff. The analytical work was confined to a determination of the total phosphoric acid and that soluble in the Wagner reagent. The data obtained follow :

	Original sample.	Separate No. 1.	Separate No. 2.	Separate No. 3.	Separate No. 4.	Separate No. 5.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total $P_2O_5$ .....	16.54	13.91	16.14	16.71	18.21	18.16
Citrate soluble $P_2O_5$ ...	11.67	6.24	10.85	12.21	13.65	14.91
Proportion of original sample		12.00	33.00	26.00	8.00	21.00

From the above analyses, it is seen that the separates four and five contain not only the highest total quantity of phosphoric acid, but also the highest available acid. It is seen that there is a regular progression in the richness and availability of the sample from the coarsest to the finest parts. The relative proportions of the different separates to the whole are shown in the table. The data lead to the inference that it may be advantageous to the manufacturer of basic slags to secure at least a partial separation, in some such manner as indicated, for the purpose of being able to place on the market a more concentrated and available fertilizing material. The annual product of basic phosphate slags now amounts to about 1,500,000 tons and the output is rapidly increasing. Up to the present time American analysts have not had occasion to examine many samples of phosphatic slags but it is certain, in the near future, that the consumption of this material in the United States will rapidly increase. It is important, therefore, that investigations be made looking to the best methods of chemical and mechanical analysis.