

## XXIV.—COMPOSITION OF AMERICAN KAOLINS.

BY CHARLES F. MABERY AND OTIS T. KLOOZ.<sup>1</sup>

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ALTHOUGH great advances have been made in recent years toward a better knowledge of American clays and suitable methods for the manufacture of ware from them, much more extended investigation is necessary, both concerning the composition of the great clay deposits and in the details of manufacture. The first and most essential information is a correct knowledge of the composition of all clays available for use. Of scarcely less importance is masterly skill in the purification of crude materials, shaping the ware and burning. In the preparation of material it is questionable whether American manufacturers can wait patiently several months for the slow processes of lixiviations and kneading that European porcelain makers have found indispensable in the production of the finest porcelain. The great porcelain factories in Europe are founded on the application of scientific skill and a personality in shaping and burning, handed down by lineal descent through many generations. Is it possible to procure for American factories scions for those ancient families, or must we wait for its perfection by our own ready facility and ingenuity?

As already mentioned, the porcelain manufacturer must be perfectly familiar with the composition of all materials within his reach. In making suitable mixtures he must have before him as one of the most essential features of composition, the proportions of free and combined silica, as well as the percentages of lime, iron, alkalis and water.

Having at hand a collection of clays, including representatives of American deposits, as well as several specimens from famous factories in Germany, it seemed of interest to compare the composition of clays from different sources. For the manufacture of the finest porcelain, the kaolin used in the Royal Berlin factory, at Charlottenburg, may be accepted as a standard of comparison. As every one knows who is familiar with the

<sup>1</sup> This work was offered by Mr. Klooz in a thesis for the degree of Bachelor of Science.

qualities of true porcelain, the products from this factory are approached by no other in the world. The composition of the kaolin used in the manufacture of this ware is shown by the following analysis of the clay, two specimens selected at different times, from great quantities within the Berlin factory.

	I	II.
Combined water .....	6.00	7.65
Silica.....	72.16	65.70
Alumina.....	20.05	24.49
Iron.....	0.10	1.03
Lime.....	1.14	0.60
Magnesia .....	0.02	0.26
Sodium oxide.....	0.12	0.23
Potassium oxide.....	0.41	0.03
Free silica.....	49.84	44.93

The different percentages in these analyses indicate that some latitude is permissible, although a high percentage of silica is evidently essential. These analyses show nearly the same composition as is given in the numerous analyses of the most celebrated clays of the German factories, especially in the low percentages of lime, iron and alkalis, and the large proportion of silica. An analysis of biscuit ware from the same factory shows nearly the same composition. Apparently the clay has the required proportion of silica without further addition :

Silica .....	68.24
Alumina .....	29.16
Iron.....	0.10
Lime.....	1.18
Magnesia.....	0.12
Alkalies.....	0.17
Free silica.....	57.50

Of the American clays, analyses showed that some contained a considerable excess of silica above the amount required for the oxygen ratio of silica to that of the alumina, 2 : 1, or the formula  $Al_2O_3 \cdot 3SiO_2$ , which is accepted in the manufacture of the best German ware ; others only a small excess of silica. Of the high silica clays, a specimen from a deposit in Maryland gave the following results :

Combined water.....	11.23
Silica .....	47.60
Alumina .....	37.38
Iron.....	1.66
Lime.....	1.50
Sodium oxide .....	0.22
Potassium oxide.....	0.34
Free silica.....	17.10

Another clay of this class is a Missouri kaolin which was analyzed :

Combined water.....	4.15
Silica .....	82.64
Iron.....	12.41
Lime.....	0.05
Magnesia .....	0.11
Sodium oxide .....	0.08
Potassium oxide.....	0.53
Free silica.....	69.45

The following analysis represents another high silica clay from Black Rock, Arkansas :

Combined water.....	3.98
Silica .....	84.24
Alumina .....	11.50
Iron.....	0.08
Lime.....	0.52
Magnesia .....	0.02
Sodium oxide .....	trace
Potassium oxide.....	0.42
Free silica.....	69.93

Another high silica clay is from Milton Hollow, Middlesex Co., N. J. :

Combined water.....	5.52
Silica .....	75.06
Alumina .....	18.32
Iron .....	0.08
Lime.....	0.80
Magnesia .....	0.14
Potassium oxide.....	0.25
Free silica.....	59.71

A specimen of clay from a deposit in Washington, Middlesex Co., N. J., also showed a high percentage of silica :

Combined water.....	2.00
Silica .....	89.16
Alumina .....	5.77
Iron.....	0.07
Lime.....	0.70
Magnesia .....	0.12
Potassium oxide.....	1.29
Sodium oxide .....	1.31
Free silica.....	80.30

A clay having nearly the same composition as the specimen from the Berlin factory, is from a deposit at Hockessen, Delaware :

Combined water.....	6.55
Silica .....	71.46
Alumina .....	21.02
Iron.....	0.08
Lime.....	0.54
Magnesia.....	0.14
Potassium oxide.....	0.33
Sodium oxide .....	0.36
Free silica.....	53.13

It should not be inferred from the foregoing analyses that all American clays are high in silica. Some of the largest and most important deposits contain very little free silica. One of the purest kaolins is found in large quantities in Indiana, and the following analysis shows its composition :

Combined water.....	15.09
Silica .....	44.23
Alumina .....	40.56
Iron .....	0.07
Lime.....	0.13
Magnesia.....	0.10
Potassium oxide.....	0.10
Sodium oxide .....	0.15
Free silica .....	2.41

A clay of somewhat similar quality is found in Northampton Co., Pa. :

Combined water.....	11.20
Silica .....	48.16
Alumina .....	37.24
Lime.....	2.00
Magnesia.....	0.29
Iron.....	1.16
Potassium oxide.....	0.25
Sodium oxide .....	0.08
Free silica.....	2.85

A paper clay from South Amboy, N. J., Middlesex Co., gave the following results on analysis:

Combined water.....	13.35
Silica .....	43.30
Alumina .....	42.45
Iron.....	0.09
Lime.....	0.34
Magnesia .....	0.10
Potassium oxide.....	0.44
Sodium oxide .....	0.08
Free silica.....	3.55

A washed clay used in the manufacture of china, from New Castle, Del., gave the following composition:

Combined water.....	12.95
Silica .....	47.42
Alumina .....	38.42
Iron.....	0.08
Lime.....	0.70
Magnesia.....	0.12
Potassium oxide.....	0.30
Sodium oxide .....	0.12
Free silica.....	4.79

A clay in Woodbridge, Middlesex Co., N. J., also used in the manufacture of ware, is nearly pure kaolin:

Combined water.....	14.34
Silica .....	44.34
Alumina .....	38.09
Iron.....	0.15
Lime.....	0.96
Magnesia .....	0.10
Potassium oxide.....	1.00
Sodium oxide .....	0.79
Free silica.....	1.33

It is interesting to compare the composition of American kaolins with a standard kaolin used in England :

Combined water .....	13.00
Silica .....	46.00
Alumina .....	40.00
Iron.....	0.33
Lime.....	0.33
Magnesia.....	0.33

Several of the clays analyzed are used in the manufacture of ware. From some of these deposits specimens have been analyzed, and the results given in the "Chemistry of Pottery," by K. Langenbeck, are not essentially different from those given in this paper.

It is evident that the wide differences in the proportions of clay and silica in American kaolins render it imperatively necessary that they be taken into account in the selection of materials for the manufacture of ware. It is also evident that the United States is not wanting in an abundance of material for the manufacture of ware equal to the best foreign production.

#### DISCUSSION.

*Wm. McMurtrie* : It is an interesting fact not brought out here, that in many of the clays of New Jersey, and I think particularly from some of the deposits represented in the tables, Prof. Geo. H. Cook reported appreciable quantities of titanitic oxide amounting to one-half per cent. more or less. The same constituent has been found in clays from other localities which I do not now exactly remember, but I have been led to believe that the existence of titanitic oxide may be expected in a good many American clays.

*W. A. Noyes* : I have analyzed a number of Indiana clays and have found titanitic oxide with but one exception. The Indiana clay given corresponds closely with one I analyzed last fall, and that particular one is free from titanitic oxide, or practically so. All the other clays, and I feel safe to say that all these clays must contain titanitic oxide.

*The President* : Does anyone know the effect of titanium on the ware ?

*A. A. Breneman*: My impression is that Seger says there seems to be a connection between the peculiar light gray of salt-glazed stoneware, a color which is unique, and the presence of titanium. That is a very interesting statement, because that peculiar form of whitish or bluish gray stoneware is very characteristic, and I see nothing in the presence of iron alone in the clay sufficiently to account for it.<sup>1</sup>

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.]

## XXV. COMPOSITION OF CERTAIN MINERAL WATERS IN NORTHWESTERN PENNSYLVANIA.<sup>2</sup>

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THE therapeutic qualities of mineral springs throughout northwestern Pennsylvania have long been recognized, and recently some of these springs, notably those at Saegertown and Cambridgeboro, have come into prominence through the enterprise of persons interested in hotels and sanitariums. The desirable qualities of these waters are doubtless dependent on

<sup>1</sup>NOTE ON TITANIUM IN CLAYS.—In the course of a discussion of Prof. Mabery's paper on American clays at the Buffalo meeting I alluded to the peculiar color of salt-glazed stoneware, and ascribed to Seger the suggestion that it was due to the presence of titanium. On referring to Seger's article (Wagner's Jahresbericht, 1883, p. 625), I find that he says that titanitic acid (13.3 per cent.) heated with a very pure kaolin to a temperature between the melting points of wrought iron and platinum fuses, and that titanitic acid is, under similar conditions, more of a flux for clay than silicic acid is. In the proportion of 6.65 per cent. of  $TiO_2$ , the mass became only semi-fused, and exhibited a dark-blue gray color. He says this color suggests the tint given by many clays when strongly heated.

Morgenroth (Wag. Jahr., 1884, 638) says, however, that rutile gives to clay ware a gray color under the glaze when impure ferruginous clays are used, but a yellow, ivory-like tint with pure clays. As rutile was used in the proportion of only 0.4 per cent., the minute proportion of iron which it carries (1.5 to 2.4 per cent.  $Fe_2O_3$ ) would have little effect.

The interpretation of these facts to explain the peculiar gray color of salt-glazed stoneware, was probably a suggestion of my own, made at the time of reading these articles a dozen years ago. It was ascribed in the course of the discussion to Seger, as my "impression."

Nevertheless, in view of the peculiarity of this color, the gray of salt-glazed ware which is uniform throughout the body and becomes more bluish in overburned pieces, and in view also of the presence of iron in the rather crude clays used for the ware, and the fact that iron alone tends to escape as volatile chloride in presence of the salt used for glazing, the suggestion is worthy of note.

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<sup>2</sup>This work, with a study of the methods of analysis, was offered by Mr. Robinson in a thesis for the degree of Bachelor of Science. Read at the Buffalo Meeting, August, 1896.