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The determination of the alumina content in diaspore and high alumina clays

W. D. Keller

THE DETERMINATION OF THE ALUMINA CONTENT IN DIASPORE AND HIGH ALUMINA CLAYS.

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WALTER D. KELLER

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THE DETERMINATION OF THE ALUMINA CONTENT IN DIASPORE AND HIGH ALUMINA CLAYS.

INTRODUCTION

The determination of the alumina in diaspore and kindred high alumina clays has been a problem which has attracted the interest of ceramists and chemists ever since a sample of Missouri diaspore was first sent for analysis to the laboratories of the Missouri School of Mines and Metallurgy in 1917.

At the outset, although these clays contain silica and silicates, the standard procedure for silicate analysis had to be modified somewhat in order to handle them. Again, although that modified method gives results that are acceptable chemically, it cannot be used for control tests in many cases because of its high cost and the excessive length of time required for the determination. Hence, there is an urgent need by those actively engaged in mining and grading, buying, or selling diaspore and burley clays for a rapid, inexpensive, fairly accurate method for arriving at the alumina content of them.

It is not unusual then that efforts have been made to devise a direct means for alumina determination. Unfortunately these have met with only limited success thus far, and at the present time most work on this problem is being done on indirect methods of estimation, some of which give promise of being fairly accurate and satisfactory.

It is the writer's intention to review in this paper the various published methods for the determination of alumina in high alumina clays and to present a new indirect one that after some months' use in industrial practice fulfills, in some measure at least, the need outlined above.

In addition, the method used by miners in the field to estimate the alumina content of the clay and grade it thereby, will be discussed in detail.

A careful search for articles on alumina determination was made by systematically examining all abstracts of the Journal of the American Ceramic Society to date, the bibliography of the Transactions of same, and books and papers on chemical analysis. It is believed that no important analytical methods were overlooked.

REVIEW OF METHODS

1. The Orthodox Chemical Wet Method.

Since the diaspore-flint series of clays appear siliceous, and do contain up to about 45 per cent. SiO_2, it would seem upon first thought that the alumina in them could be determined by following the standard procedure for the analysis of silicate rocks as outlined by Hillebrand.[1] However it was found by Thornberry, who probably was the first chemist to analyze Missouri diaspore clay, that fusion in Na_2CO_3, the initial step in the usual silicate analysis, would not break down and dissolve diaspore. It was necessary to modify the older silicate analysis procedure by using NaOH instead in the dissolving flux, and this change, proposed by Thornberry[2], is still being made in diaspore analysis. After the fusion the analysis proceeds essentially the same as the standard one for silicates.

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[1] W. F. Hillebrand, The Analysis of Silicate and Carbonate Rocks, U. S. Geol. Survey Bull. No. 700.

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[2] M. H. Thornberry, Method of Analyzing Diaspore Clay, Jour. Amer. Cer. Soc., 6, 1261-1262, (1923).
Same author, A Treatise on Missouri Clays, Bull. of Missouri School of Mines and Metallurgy, Technical Series, Vol. 8, No. 2, Feb. 1925. (Gives complete clay analysis procedure in detail.

The objections to the determination of alumina by this method are its cost, about Six Dollars per sample, as a minimum, and the time for its completion, at least two days. Not many routine control tests can be run on a low-priced commodity when the cost of each test is as much as six dollars. Again, if material is to be tested before purchasing, shipping, or manufacturing, and information as to its meeting specifications is not available within at least two days after sampling, the time elapsed is so long, in many cases, that the information is of no value when received, or, if the material be held until results of the test are received the delay will be so expensive as to be prohibitive.

There is no question at the present time but that this old established method will be the stand-by and standard of comparison for other methods, but in addition, a faster and less expensive one, even though slightly less accurate, is also needed.

2. A Less Well Known Method Using 8-Hydroxyquinoline.

A wet method for a rapid direct determination of alumina was outlined in 1928 by Josef Robitschek.[3] He claims that determinations can be made in one and one-half hours, and his data, although extremely limited, indicate an accuracy comparable to the long wet method.

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[3] Josef Robitschek, The Use of 8-Hydroxyquinoline for the Chemical Analysis of Silicates, Jour. Amer. Cer. Soc., 11, 587-594, (1928).

His method involves the usual fusion, and solution of the fused cake in acid, then precipitation of the alumina with an 8-hydroxyquinoline-acetic acid reagent, followed by washing and re-dissolving. An excess of standardized potassium bromide-bromate solution is added to the dissolved precipitate and the surplus of bromine which has not been consumed by the aluminum salt is back titrated with a solution of $Na_2S_2O_3$, after potassium iodide has been added. The standard bromide-bromate solution is quantitatively consumed by the aluminum salt and the amount of it (aluminum salt) present can be calculated readily.

It is obvious that this is a quick determination and it is hoped that American ceramic laboratories will give it a thorough trial. Robitschek reports results on only 2 clays of 29.8 per cent. and 37.8 per cent. alumina content, and on a fire brick containing 41.3 per cent. alumina. Inasmuch as no more data by Robitschek, or either data or comments from laboratories doing high alumina clay analysis using this method, are available, the writer must remain non-commital on it. It is quite evident, however, that more work must be done on the method before it will meet with general approval. The high price of 8-hydroxyquinoline in 1928, $14.00 per 100 grams, will tend to hinder extensive work with it. It is quite probable, as was pointed out, that the price is high simply because there has been practically no demand for the chemical, and that it, as was the case with dimethylglyoxime, will be sold at a much lower figure if a market is established.

Incidentally, a short direct method is also described in

Robitschek's article for the determination of alkalies, and this should also be investigated further.

3. Indirect Methods Utilizing Physical Properties.

(a) Field Estimation. Non-technical, non-laboratory.

At the present time practically all of the diaspore and burley clay mined and shipped from that district is graded by workmen in the pits. Their method of estimation of the alumina content, although crude and non-technical, is surprisingly efficient. Its value should not be under-rated. The men, after familiarizing themselves with a few characteristic samples that have been analyzed, grade the clay readily to within 5% of the actual alumina content.

They use only the physical properties of the clay and characteristics dependent upon them, which include the blackish mark left on the clay by steel tools, such as the auger, the pointed wedge "gad," and the pick, when reducing the size of the boulders; the feel of the clay, whether rough or slick; the way it breaks, i.e., fracture; the sound given off when struck by a tool; the amount of "shot," oolites, or burls present; and, to a lesser extent, the grain; the way it "chews," i.e., the abrasive action when ground between the teeth of the workman; and the "weight," specific gravity, of the boulder.

These characteristics are indicative of the alumina content of the clay as follows:

The "marking" or "blacking" of the clay upon tooling.

A dark gray to black, or blue-black tool mark is left upon a good diaspore clay when split with a pick or gad (a steel wedge), or cut with an auger. The intensity of the color of this mark is dependent upon the abrasive action and hardness of the clay which, in turn, is dependent upon the alumina content. An explanation follows:

Diaspore clay contains a varying amount of mineral referred to as the mineral diaspore (the correctness of its name is questioned by some students), the richest clay containing the most diaspore, whereas the poorer clay, i.e., lower in alumina, contains in addition, as an impurity, kaolin-like bonding material. The hardness of diaspore, according to Dana, is 6.5-7, in contrast to the hardness of kaolin, which is 2.2-5. Hence, as the quality of the diaspore clay becomes higher, the quantity of the harder pure diaspore mineral that it contains increases, its abrasive action becomes more pronounced, and the "streak" of the steel tool will be darker. Experience has shown that a dark mark begins to be left upon damp clay when the alumina content is about 60 per cent. or above. A pronounced black is left upon clay containing 68-70 per cent. alumina, and a very deep blue-black color upon the select clay containing 72 per cent. alumina and above. A certain amount of practice in judging the depth of color and its corresponding alumina content is essential for close estimation. Dry clay of the same quality does not retain the mark nearly so well as damp clay, and its alumina content can not be estimated accurately by this method. However, in the workings, where the clay is damp from ground water, the writer finds this method to be one of the most reliable means of estimation.

In some pits, the grader carries a small geologist's hammer, the head of which he rubs over the clay, and determines the quality from the mark left. Clay shippers and buyers often use the steel of their pocket knives to "mark" with when estimating alumina content.

Caution must be observed when testing low grade clay by this marking method, because a gray or darker colored clay, when rubbed with a harder substance, will, in many cases, crush or pack to a darker color than the surrounding material. This darker color is, of course, not referable to the abrasive mark and can easily be distinguished from the other when this difference is kept in mind. It should also be noted that, altho first grade diaspore clay possesses a hardness of over 5.5, it is usually more friable than the second grade, which is softer, but it is not crushed as easily. Friability and hardness should not be confused.

"Feel" of the Clay.

Diaspore clay is rough and harsh to the feel (touch) regardless of its texture. Flint clay has the slickest feel because of its extremely fine grain and smooth conchoidal fracture. The feel of burley and second grade clay is intermediate between the extremes. Good diaspore clay, in fact, is sometimes spoken of as the "rough" or "rough clay" because of that physical property.

The Way the Clay "Breaks," i.e., Its Fracture

This is another valuable and very reliable distinguishing characteristic. The best conchoidal fracture, an excellent one, is developed in the flint clay, containing about 40 per cent. alumina. This "slick" break continues until clay reaches about a 55 per cent. alumina content at which the conchoidal break gives way to a more hackly fracture. Above 65 per cent. alumina, and particularly above 70 per cent., the fracture is quite rough. Even in very fine textured clays the fractured surface on first quality diaspore is rough.

The Sound Given Off When Struck by a Tool

First grade diaspore when being gadded or picked gives off a dead sounding, cushioned plunk in contrast to a higher pitched clink emitted by burley or second grade clay when tooled. The rebound from a tool striking inferior clay is greater than that when working in the best clay. Perhaps the greatest difference is noticed above and below 65 per cent. clay. Many times a pit hand can classify a lump of clay before it is even broken open simply by noting its action when tooled. This judgment becomes second nature with those of long experience at mining.

The Amount of "Shot," Burls, Oolites Present

The quantity of the small concretionary diasporitic particles scattered thruout the body of clay is a good criterion for alumina estimation but operates in opposite ways depending upon whether the matrix is poor or good clay. A flinty fracturing clay with about 10 per cent. of its surface dotted with oolites usually contains 45 per cent. alumina as a minimum. As the number of oolites increase the quality of the clay increases until the alumina content reaches 60-65 per cent. In other words, the quality of a burley of poor second grade clay varies directly as the quantity of oolites in the flint-like matrix. With the first grade diaspore, the rough fracturing clay, the opposite holds true. Diaspore clay that is best, that containing in excess of 70 per cent, and particularly 72 per cent. alumina, will contain few if any oolites. As 5 to 10 per cent. of the surface of diaspore becomes oolitic the alumina content will drop to 67-68 per cent.

The "Grain" of Clay

Flint clay and the matrix of burley clay are dense and very fine-grained, diaspore is generally coarse-grained. Altho some diaspore is so fine-grained as to resemble chalk its appearance is always "rough" in contrast to the fine-grained, flinty surface of the poorer clay. Diaspore, in many instances, is quite porous, and this aids in lending a coarse-grained appearance. Clay occurring at the surface of pits (surface boulders) is markedly porous. Perhaps this is due to cavities left thru leaching of impurities. It may be noted here that the surface boulders characterized by their brown iron-oxide stained surface, usually contain in the neighborhood of 70 per cent. alumina. The idea that they are superior to all clay found in the same pit has been found to be erroneous. Clay lying immediately below the surface boulders has, in several instances, been found to run higher in alumina than the surface boulders themselves. Surface boulders then may be always considered first grade clay, but not necessarily always the best. Diaspore clay, in addition to being more porous, is likewise far more permeable to water than burley clay. Strata of diaspore in a pit face or runway will remain damp and dark due to the movement of water to the surface instead of drying, as the impervious flint or burley does.

The Way Clay "Chews"

Diaspore clay, when ground between the teeth, retains its abrasive action, due to its inherent hardness, even when finely pulverized, but flint or burley, because of its high content of kaolin-like material, is quickly ground up and "goes to water" in one's mouth.

Altho diaspore has a higher specific gravity (3.3-3.5, Dana) than kaolin (2.6-2.63), a boulder of diaspore is usually lighter in weight than one of equal size of burley or second grade because it (diaspore) is more open textured and porous. This property is less important and is not commonly used in clay grading.

As a means of summary of the ways that this non-technical field estimation of the alumina content of clay is made, a table has been prepared which, if followed, will aid in classifying the clay.

Scheme for the Estimation of the Alumina Content of a Field Specimen

A damp sample from the pit is to be estimated. It is broken to expose a fresh surface.

Surface shows:

Rough, hackly fracture. Marked with steel.--Over 60 per cent. Al_2O_3. Probably diaspore.

Slick, conchoidal fracture. Does not mark with steel. --Under 60 per cent. Al_2O_3. Probably burley or "seconds."

Surface examined more closely shows:

Typical conchoidal fracture. Few or no oolites. Less than 45 per cent. Al_2O_3.

Conchoidal fracture but up to 20 per cent. oolites. 45 per cent. to 50 per cent. Al_2O_3.

Oolites abundant (up to 50 per cent.) but flinty fracture of matrix between them 50 per cent. to 55 per cent. Al_2O_3.

Oolites predominate, or an irregular fracture, not typically conchoidal. Will not blacken when rubbed with steel. 55 per cent. to 60 per cent. Al_2O_3.

Rough fracture. Rough surface. Retains light non-uniform black mark when rubbed with steel. 60 per cent. to 65 per cent. Al_2O_3.

Rough fracture. Entire absence of "slick" break. Matrix crushes fairly easily to a powder. Powder often seen on surface. Marks well with steel. Some oolites present. 65 per cent. to 70 per cent. Al_2O_3.

Rough fracture. Usually friable. Harsh feel. Few oolites. Prominent uniform black mark retained when rubbed with steel. 70 per cent. to 72 per cent. Al_2O_3.

Same as above but deep blue-black steel mark. Over 72 per cent. Al_2O_3.

3 (b) Laboratory or Semi-laboratory Methods Utilizing

Physical Properties

The difference in physical properties of clays varying in alumina content is likewise used in laboratory methods of moderate precision to determine the alumina content of the clay. The tests employed may be made in a well equipped plant laboratory, or, since apparatus of highest accuracy and delicacy is not essential, a small field laboratory may be set up at the pit and determinations made there. The difference in specific gravity between that of diaspore, 3.4, and that of kaolinite, 2.6, has been taken advantage of in making this type of determinations.

The idea was first brought to print by Wherry[4], who in describing the identification of diaspore, suggested crushing the unknown clay to 60 mesh and shaking in a bromoform solution of 2.8 specific gravity. The kaolinite, calcite, quartz, etc., will float, whereas diaspore and some of the iron and titanium minerals sink in this liquid. The presence of diaspore is indicated by a light-colored, heavy residue, the other minerals usually being dark.

H. S. McQueen[5], in an unpublished manuscript, proposed the separation of diaspore from surrounding lower gravity clay by using acetylene tetrabromide, sp. g. 2.95, and, having weighed the clay originally and the residue diaspore after separation, calculated the percentage alumina content of the sample. His plan was to crush the clay, dry it, and shake up with acetylene tetrabromide in a separatory funnel and draw off the heavy residue which could readily be dried and weighed.

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[4] E.T.Wherry, Field Identification of Diasporite, Am. Mineral., 3, 154, (1918).

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[5] Assistant State Geologist of Missouri.

It is doubtful if this method was used to any considerable extent, although it appears to be quite practical.

The most recently published work utilizing the high specific gravity of diaspore is by Phelps and Hughes[6]. Their method is to crush the diaspore to 40 mesh, dry, and weigh up 20 grams. This sample is put into a special bottle equipped with a special stopper, and containing a standard uniform volume of water. After thoroly wetting the clay by shaking, a graduated plunger is introduced thru the stopper and immersed until sufficient water is displaced by it to overflow the top of the stopper. The depth of immersion is read on the graduated plunger and this figure referred to an empirical graph having alumina percentage plotted against plunger readings. The graph was prepared by drawing a curve thru points representing plunger readings of clays plotted against the analyzed alumina contents of the same.

This method is sound theoretically for there is quite obviously a difference between the volume of a 20-gram sample of high alumina, high density diaspore clay and that of a low alumina, low density flint clay sample of the same weight,and more of the plunger will have to be introduced to fill the bottle when it contains high density clay than when the sample

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[6] Stuart M. Phelps and A. C. Hughes, A Rapid Method for the Estimation of the Alumina Content of Diaspores and High Alumina Clay, Jour. Amer. Cer. Soc., 13, 1-4, (1930).

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is of low density. The relationship between the density of the clay and its alumina content is sufficiently constant to permit the fairly accurate calculation of one from the other.

A slight error, as one would expect in an indirect method, is usually present in the Phelps-Hughes rapid determination. A study of their results shows that:

	30	per cent.	of	the	calculated	values	are	0-1%	in	error
	27	"	"	"	"	"	" "	1-2%	"	"
Summing	57	"	"	"	"	"	"less than	2%	"	"
	43	"	"	"	"	"	" are over	2%	"	"

The desirable features of this method are that, (1) the time required for determination is small, only an hour being needed for grinding and drying and four or five minutes for the actual determination, (2) the apparatus is not delicate nor complicated, (3) samples may be tested in the field immediately after quarrying.

On the other hand, it is often not desirable to attempt to do precise analytical work in the field where quantity production is the goal, nor to equip a laboratory, even crudely, there. Also it might prove quite expensive to keep a man capable of making accurate tests at such work exclusively in the field, unless he has enough to run to take all of his time.

4. Indirect Methods Using Chemical Analysis.

Forbes[9], in 1928, suggested that the alumina content

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[9] C. R. Forbes, Winning of Missouri Diaspore, Burley, and Flint Clays, Jour. Amer. Cer. Soc., 11, 204-214, (1928).

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of diaspore could be found, not necessarily by its own lengthy determination, but indirectly, by a calculation involving the silica content and loss on ignition. He first determined the usual amount of impurities in the clay from a pit and assured himself that alkalis or other deleterious substances were not present in excess. Then he added the average percentage of the impurities of the clay to the determined silica and ignition loss of a sample and subtracted that sum from 100%. The remainder was the calculated alumina content. This method has the advantage that it is faster than a straight alumina determination because silica and ignition loss can be obtained quicker, but on the other hand, the accuracy is much less and the cost about the same. It is doubtful if Forbes' method is being used extensively at the present time.

4 (a). A new indirect chemical method described.

A fact of considerable importance was brought forward when it was found that a definite relationship exists between the silica and alumina contents of diaspore and burley clays and that this relationship is sufficiently constant to be expressed mathematically. This being true, a calculation of the alumina content can be made with fair accuracy from an analysis for silica alone, thereby dispensing with the more lengthy alumina determination and cutting the cost of analysis into approximately half, since SiO_2 can be determined in a small fraction of the time and at a third the expense of Al_2O_3.

The mathematical formula expressing this calculation and relationship was developed by Dr. M. E. Holmes, and its excellent agreement with actual analyses is shown by the graph plotted by the writer. The development of the formula is given below.

It has been commonly believed for some time that diaspore and burley clays are a mixture of diaspore, $Al_2O_3.H_2O$, and kaolinite, or a like mineral having a composition essentially $H_4Al_2Si_2O_9$, and some other minerals as impurities. The indications are that this belief is the truth. Then, when the sample of diaspore or burley clay is analyzed the silica that is found will be that which was in the kaolinite, and therefore for each per cent. of that SiO_2 present there will be .85% of Al_2O_3, the ratio of 2 SiO_2, 120.2, to Al_2O_3, 102.2, which are present in the kaolinite molecule in such proportion. Expressed in a different way, .85 x % SiO_2 = % Al_2O_3 in kaolinite.

Similarly, the quantity of kaolinite in the clay sample is calculated from the ratio 2 SiO_2 : $H_4Al_2Si_2O_9$ which is 120.2 : 258.1, or 1 : 2.15. Then 2.15 x % SiO_2 = % kaolinite.

The diaspore in the clay is equal to 100% - % kaolinite or 100% - 2.15 x % SiO_2. But diaspore contains 85% Al_2O_3. Hence, the Al_2O_3 in the diaspore will be .85 (100 - 2.15 x % SiO_2). The total alumina content of the sample can be expressed:

$$\% \; Al_2O_3 = .85 \times \% \; SiO_2 + .85 \; (100 - 2.15 \times \% \; SiO_2)$$

The graph of this equation is shown by the dotted line AA on Graph No. 1. This line, however, does not fall on any of the plotted actual SiO_2-Al_2O_3 analyses, all of which lie below. That is the case because so far theimpurities in the clay have been neglected. A cursory examination of a few diaspore analyses shows that about 5 per cent. of impurities such as iron oxide, lime, magnesia, titania, alkalis, etc., are present. A more accurate determination of the amount of impurities present is necessary, and this was made by taking the average of the deviations of calculated alumina content from the actual alumina content of 165 analyses of diaspore and burley clays. It was found to be 5.1%.

The method used in determining the average deviation from the 165 analyses is shown by the short table below:

Sample	Actual SiO_2 Content	Actual Al_2O_3 Content	Al_2O_3 Calculated from the formula given above	Correction
1	19.45	62.71	65.98	-3.25
2	10.56	70.26	74.67	-4.41
3	21.05	59.90	64.43	-4.53
4	25.66	52.43	59.89	-7.46
5	22.75	55.33	62.42	-7.07
6	15.42	62.31	69.93	-7.62
7	13.50	66.65	71.83	-5.18
8	27.80	52.06	57.06	-5.86
9	34.66	45.43	51.11	-5.61
10	26.06	54.34	59.52	-5.18
11	23.38	56.26	62.15	-5.88
12	14.88	66.63	71.38	-4.75
13	39.10	40.66	47.72	-7.06
14	16.33	63.27	69.03	-5.75
15	32.80	47.62	57.36	-5.32
16	20.80	60.08	65.51	-5.43
17	39.58	43.25	46.30	-3.05
18	29.28	49.97	56.38	-6.41
19	18.31	60.86	67.10	-6.24
20	35.06	45.02	50.73	-5.71
21	31.70	50.24	54.00	-3.76
22	7.85	73.89	77.32	-3.43
23	8.31	72.15	76.87	-4.71
24	31.56	48.83	54.15	-5.32
25	17.89	62.30	67.52	-5.22
26	8.27	72.27	76.84	-4.67
27	6.35	73.61	78.70	-5.09
28	10.90	69.76	74.35	-4.59
29	12.59	68.81	72.69	-3.88
			Average	-5.12

To repeat, the calculated Al_2O_3 is, on the average, 5.1% higher than the actual Al_2O_3. This deviation must be applied as a negative correction factor, -5.1, to the formula, after which it represents the SiO_2-Al_2O_3 relationship of the average clay. The corrected formula then becomes:

$$\% \; Al_2O_3 = .85 \times \% \; SiO_2 + .85(100 - 2.15 \times \% \; SiO_2) - 5.1$$

Line BB is the graph of this equation. It occupies practically a median position with reference to the results of the analysis of 381 diaspore and burley clays which are shown plotted with Al_2O_3 content as abscissa and SiO_2 as ordinate. The unquestionable applicability of the mathematical equation is obvious. It takes on still more weight when it is recognized that this set of analyses is absolutely representative, and is probably the most extensive one of its kind in existence.

Furthermore, the analyses are not chosen, but include all of those made of the diaspore and burley clay sent in to the Missouri Clay Testing and Research Laboratories over a period of several years excepting that those above 4% Fe_2O_3 and 3.5% alkalis (combined) were rejected. This rejection should be made because clay that high in flux would not be used in the manufacture of refractories. Hence the data are comprehensive, practical, and reliable.

A check on the accuracy of the results obtained by this indirect method shows that:

64.3 per cent. of the calculated values are 0-1% in error
24.4 " " " " " " " 1-2% " "
Summing 88.7 " " " " " values less than 2% " "
and 11.0 " " " " " values are 2-3.5% " "

Only a scattered half dozen are sufficiently inaccurate to be worthless.

This method gives greater accuracy than the Phelps-Hughes method, although the two should hardly be compared. One (Phelps-Hughes method) is adapted to field use whereas the other is strictly a laboratory analysis. With the latter the men at the mine are not concerned with fine analytical technique or apparatus. The sampler there simply sends his clay to the chemist for a silica determination. Upon receipt of the results he refers them to the graph and reads the corresponding Al_2O_3 content. The method is rapid, accurate, and inexpensive.

The writer wishes to acknowledge again the courtesy of the staff of the Missouri Clay Testing and Research Laboratories in making available the results of their high alumina clay analyses. The analytical cost alone of them is in excess of $2500, and this combined with the field work necessary to their collection would make an investigation of this kind, for its own sake, entirely out of question.

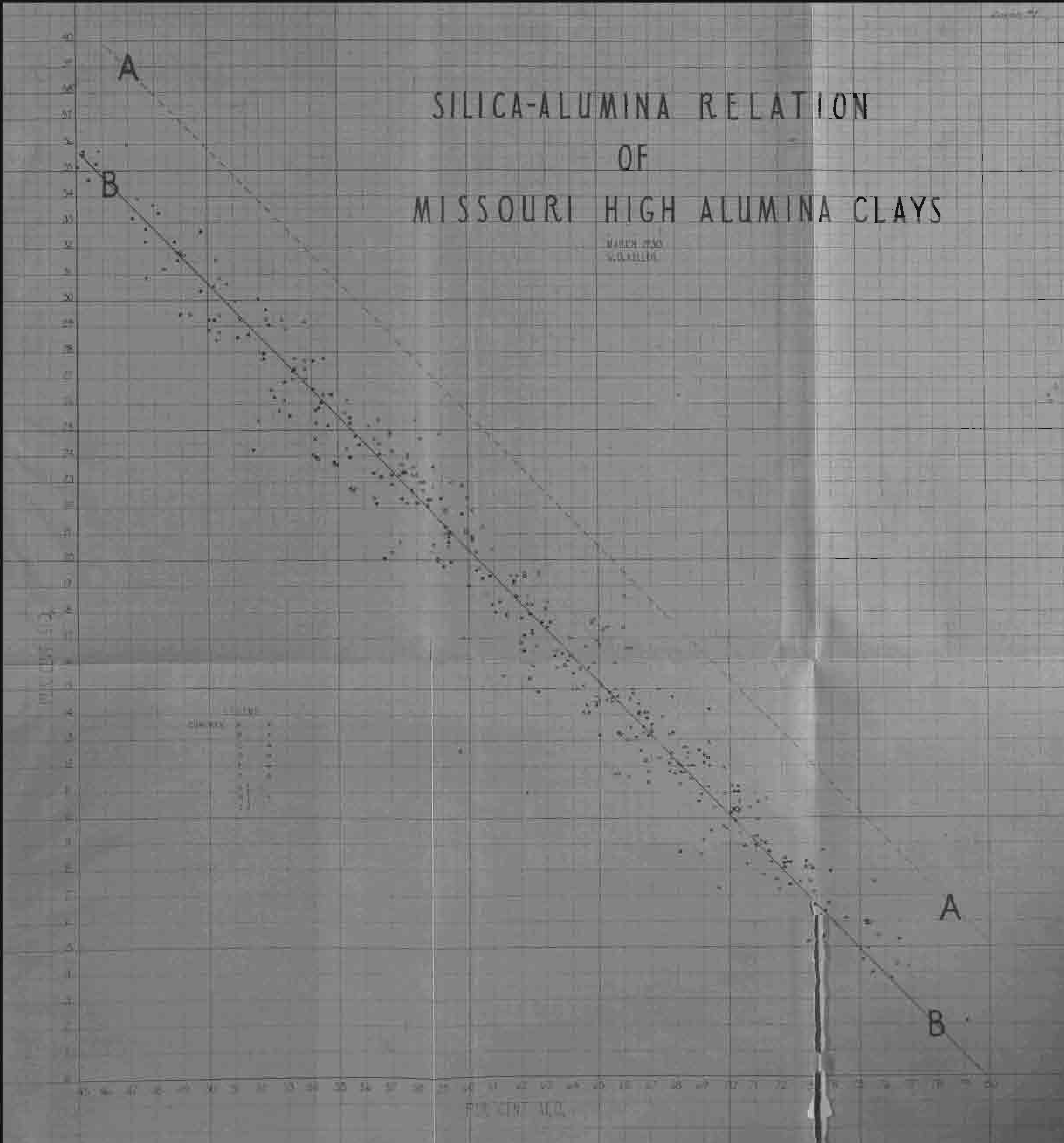
4 (b). A modified SiO_2-Al_2O_3 method.

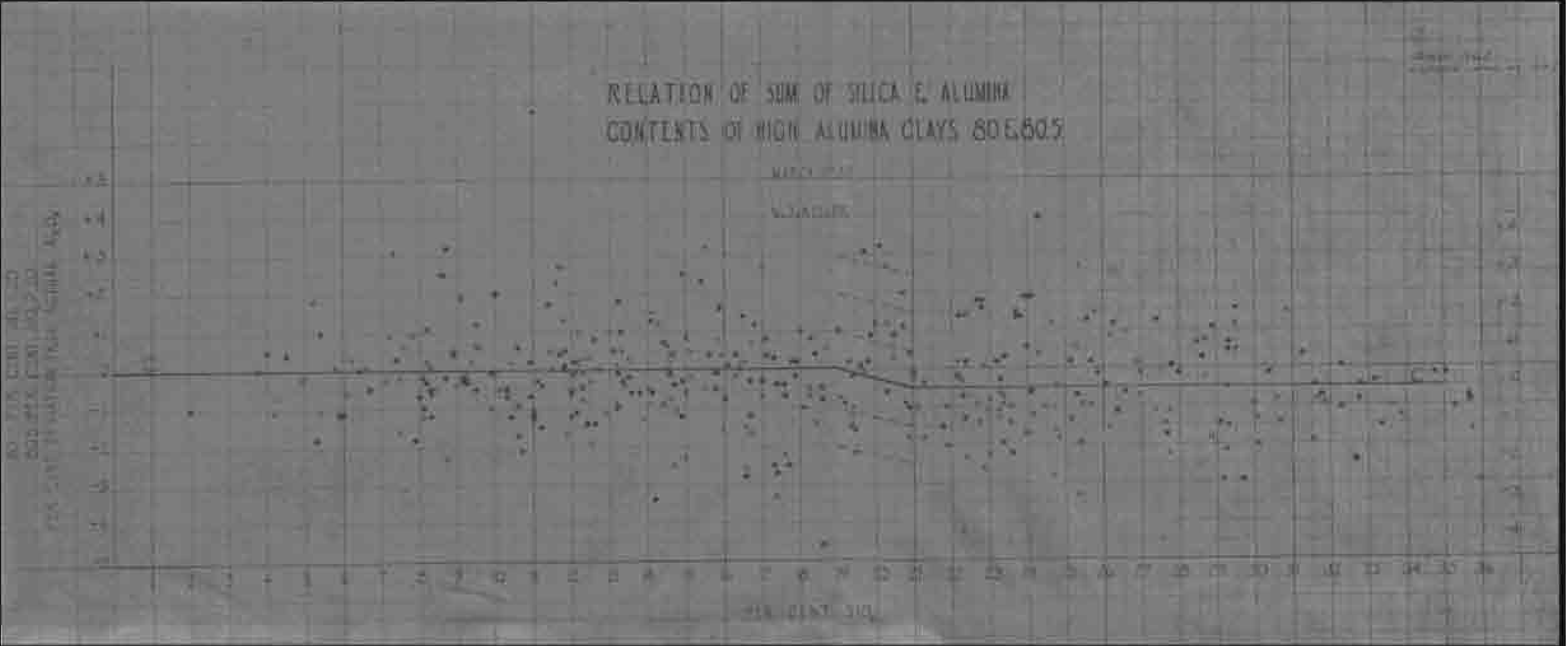
A more or less empirical but simpler method of obtaining the Al_2O_3 content from the SiO_2 of high alumina clays involving less calculation and no graph, was formulated by the writer.

The SiO_2 content is simply subtracted from 80 in case SiO_2 is less than 20%, and subtracted from 80.5 in case SiO_2 is over 20%, the remainder in the subtraction in either case being the Al_2O_3 content. As will be shown later, the accuracy of this method is essentially the same as that of the one using the mathematical formula.

The theory substantiating the subtraction method is as follows: Theoretically pure diaspore contains 85% Al_2O_3 and 15% H_2O. It was shown that the clays under discussion contain about 5% impurities. This subtracted from 85% leaves 80% which represents the sum of the SiO_2 in the kaolinite and the Al_2O_3 in the mixture of kaolinite and diaspore. Hence, 80 - % SiO_2 = % Al_2O_3. Kaolinite contains 14% H_2O and 86% $SiO_2 + Al_2O_3$ in kaolinite. The clays lower in alumina, the burleys, contain more kaolinite than diaspore. Therefore, the SiO_2 in these is subtracted from 80.5. As was previously stated, 80.5 is used as the subtrahend when SiO_2 is greater than 20%, these clays being in the burley class.

The deviations of the calculated alumina content from the actual alumina content by the subtraction method are shown in Graph No. 2. (Same analyses as in Graph No. 1). Line CC represents exact agreement--zero deviation. It also shows the positive applicability of this method. Upon inspection it is seen that:


SILICA-ALUMINA RELATION
OF
MISSOURI HIGH ALUMINA CLAYS
A
B
A
B


RELATION OF SUM OF SILICA & ALUMINA
CONTENTS OF HIGH ALUMINA CLAYS 80&60.5
PER CENT SiO2

64	per cent.	of	the	calculated values are...............	0-1%	in	error
24.2	"	"	"	calculated values are...............	1-2%	"	"
Summing 88.2	"	"	"	calculated values are less than.....	2%	"	"
and 11	"	"	"	calculated values are...............	2-3.5%	"	"

The advantage of this method is that the calculation can be done in the field, "in one's head," without graph or pencil.

The last two methods have been tested out and used by the writer in actual practice, and have been found highly satisfactory.