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Study of the substitution of barite for barium carbonate in a whiteware body suitable for brick manufacture

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STUDY OF THE SUBSTITUTION OF BARITE FOR BARIUM CARBONATE IN A WHITEWARE BODY SUITABLE FOR BRICK MANUFACTURE

By

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A

THESIS

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The writer wishes to express his appreciation to Professor C. M. Dodd for his many helpful comments and criticisms during this research.

INTRODUCTION

Some years ago a method of manufacturing white brick from Georgia Kaolin and apatite rock was developed[1]. This was successful for supplying an attractive white brick to the southern trade, until difficulties were encountered in securing apatite rock of sufficiently high grade to insure the continuance of manufacture of the brick.

There is a possibility that other deposits of that rock in close proximity to the plant could be found, but this possibility has evidently been investigated, because the plant was closed while there was still a demand for their product.

With the foregoing facts at hand, a study was made of the utilization of an auxiliary flux to replace the apatite rock. A commercial brick was developed[2], wherein eight (8) per cent of this flux, with forty-two (42) per cent potters flint and fifty (50) per cent Georgia Kaolin was used.

(1) Ref. - Stull and Bole

(2) "Utilization of Feldspar - Alkaline Earth Eutectics as Vitrifying Agents for Georgia Kaolins" Thesis by C. M. Dodd, O.S.U. (1927)

The barium carbonate used in the auxiliary flux was excessive in cost, and so it is proposed to see if barite in some form, which is comparatively cheap, can be substituted for the barium carbonate. With this object in view, it is proposed to make a study as outlined below.

Barite is found in abundant quantities in the United States, Missouri being the leading producer of this mineral. Crude barite, in 1930, was quoted at seven to eight dollars per short ton in Missouri, compared with twenty-three dollars per short ton for floated barite, and forty-seven dollars per short ton for barium carbonate[1].

Barium oxide has not been used extensively in ceramic bodies in the past, as the vitrification is short, and it is a violent flux. It was also thought to weaken the body[2], if present in appreciable quantities.

While crude barite has a slight percentage of iron, it is not enough to affect the color of white brick. Crude barite from Missouri has ninety-five (95) per cent barium sulfate and one

(1) Mineral Resources of the U.S. (1930 p. 291-301, by Santmyers and Stoddard

(2) "Non-Plastic Ceramic Materials" - R. Niederleuthner (Julius Springer, Berlin)

(1) per cent iron. The floated barite is washed and ground to pass 200 mesh.

The body used was of the approximate composition of that recommended by Dodd[2]; that is, fifty (50) per cent Georgia Kaolin, forty (40) per cent flint and ten (10) per cent flux, in various combinations

PURPOSE OF RESEARCH

In this research it was desired to investigate the possibilities of substituting barite for barium carbonate in whiteware body suitable for white brick manufacture. The effect of fritting the fluxes before introduction was studied and compared to unfritted bodies of the same composition. Bodies using crude barite were compared with bodies using floated barite.

METHOD OF PROCEDURE

Materials Used.

The materials used and their sizing are as follows:

Georgia kaolin	20 mesh

Sandy kaolin	10 mesh
Buckingham feldspar	200 "
Ottawa sand	Grain size (20-30 mesh)
South Carolina silica	100 mesh
Magnesium carbonate	200 "
Calcium carbonate	200 "
Floated barite	150 "
Crude barite	60 "
Potters flint	150 "

Sizing of Materials.

The materials were ground to the sizes shown above, where necessary. The Georgia Kaolin was ground to size with a mortar and pestle. The crude barite was crushed in a jaw crusher, and then given a secondary crushing in a roll crusher. The barite was then screened through 60 mesh on a Great Western Manufacturing Company Gyrating Riddle.

Mixes.

The mixes were as follows:

(1)	Georgia kaolin	49.579 %
	Ottawa sand	39.600
	Buckingham feldspar	6.583
	Calcium carbonate	1.140
	Magnesium "	.228
	Barite	2.810

(2) (Body)

Georgia kaolin	49.579 %
Ottawa sand	39.600
Frit	10.761

(Frit)

Buckingham Feldspar	61.17 %
Calcium carbonate	10.59
Magnesium "	2.12
Barium sulfate	26.11

(3)

Georgia kaolin	42.16 %
Sandy kaolin	28.60
Frit	29.24

(Frit)

Feldspar	21.886 %
Calcium carbonate	3.766
Magnesium "	.707
Crude barite	7.704
Potters flint	65.937

(4) Body

Georgia kaolin	50.54 %
Ottawa sand	20.22
Frit	29.24

(Frit)

Buckingham feldspar	21.886 %
Calcium carbonate	3.766
Magnesium "	.707
Floated Barite	7.704
Sand	65.937

(5)

Georgia kaolin	50.000 %
South Carolina kaolin	40.000
Buckingham feldspar	6.583
Calcium carbonate	4.420
Magnesium "	.684
Crude barite	8.430

Fritting.

The fluxing ingredients were placed in fireclay crucibles, which were then heated up to melting temperature in an oil fired pot furnace. A hole was drilled in the bottom of each crucible, through which the melt escaped and dropped through a hole in the bottom of the furnace, and into a pan of water. This was to quench the melt and crack it, for greater ease in grinding. The material was then ground in a ball mill to 150 mesh in one case, and 60 mesh in the others. Note that some of the iron was drawn from the crucible, but was easily separated from the rest by hand picking.

Forming.

In all cases the dry ingredients were placed in a ball mill for a short time, and then sifted through a 40 mesh screen to insure thorough mixing.

Body No. 1 - Two bodies were made up, one using crude barite, and one using floated barite. A two thousand gram batch was made up of each mix. Water was added until the desired plasticity was reached, and then bars 1" x 1" x 6" were hand molded in a brass mold.

Body No. 2 - Two bodies were made up of this composition, one with crude barite and one with floated barite. The fluxing ingredients were fritted, and then ground dry in a ball mill to pass 60 mesh. The frit was added to the clay and silica, and water added until plasticity was reached. The bars were formed as before.

Body No. 3 - This procedure was the same as for body No. 2, except that only one body was made up, using crude barite.

Body No. 4 - Floated barite was used in this body. 2000 grams were made up, according to the procedure followed in making up bodies No. 2 and No. 3.

Body No. 5 - South Carolina silica was used in making up this body. The bars were made according to the procedure for body No. 1.

Drying and Firing.

The bars were dried bone dry, and then fired to cone 6, in an oil fired laboratory muffle kiln. The ware was fired at the rate of 100° C. per hour, to 500° C. It was then fired at about 80° C. per hour to 900° C., and the rate was increased to 150° C. per hour to cone 5 down. The temperature was held constant, and cone 6 was soaked down. The purpose of this was to insure equal distribution of the heat throughout the setting.

Tests.

The following formulae were used in computing the data present.

$$\text{Modulus of Rupture} = \frac{3 \times Pl}{2bd^2}$$

P = Load in pounds
l = Length of span in inches
b = Breadth in inches
d = Depth in inches

$$\text{Drying Shrinkage} = \frac{\text{Plastic length} - \text{Dry length}}{\text{Dry length}}$$

$$\text{Fired Shrinkage} = \frac{\text{Dry length} - \text{Fired length}}{\text{Dry length}}$$

$$\text{Absorption} = \frac{\text{Wt. fired} - \text{Saturated Wt.}}{\text{Wt. fired}}$$

DATA

TABLE I

Body (1) a - Crude Barite Water of Plasticity 23.53%

Member	Percent Drying Shrinkage	Percent Fire Shrinkage	Percent Total Shrinkage	Modulus of Rupture #/sq. in.	Percent Absorption
1	4.16				19.30
2	4.16	2.71	6.87	313	19.10
3	3.71	2.81	6.54	229	18.80
4	3.71				18.90
5	3.73	2.49	6.22	280	19.40
6	3.73	2.70	6.43	274	19.60
Average	3.87	2.68	6.52	274	1910

Body (1) b Floated Barite Water of Plasticity 22.58%

1	3.31	3.31	6.62	379	18.20
2	2.88	2.68	5.56	386	18.40
3	2.88	3.29	6.17		20.00
4	4.16	2.50	6.66	408	19.30
5	2.88	2.47	5.35	357	18.70
6	4.16	2.92	7.08	360	19.60
7	4.16				18.70
8	4.16	2.92	7.08		18.90
Average	3.57	2.73	6.42	378	18.70

TABLE II

Body (2) a Crude Barite Water of Plasticity 22.00%

1	4.61	2.51	7.11		17.90
2	2.46	2.87	5.33		18.50
3	2.88	3.29	6.17	487	17.80
4	4.16	3.34	7.50	461	18.70
5	4.61	2.30	6.91	498	18.10
6	3.73	2.08	5.81	444	17.30
Average	3.74	2.73	6.47	443	18.10

TABLE II (Cont'd)

Body (2) b Floated Barite Water of Plasticity 22.75%

Number	Percent Drying Shrinkage	Percent Fire Shrinkage	Percent Total Shrinkage	Modulus of Rupture #/sq. in.	Percent Absorption
1	4.16	1.88	6.04	318	16.50%
2	4.16				17.00
3	3.73	2.08	5.81	333	17.60
4	3.73	2.08	5.81		14.90
5	3.09	2.27	3.36	372	18.20
6	4.16	2.50	6.66	302	17.70
Average	4.01	2.16	5.54	331	17.00

DATA

TABLE III

Body (3) Water of Plasticity 26.5%

Member	Percent Drying Shrinkage	Percent Fire Shrinkage	Percent Total Shrinkage	Modulus of Rupture #/sq. in.	Percent Absorption
1	4.82	4.91	9.73		12.50
2	3.95	5.26	9.21		12.00
3	3.95	5.46	9.41	1004	12.00
4	3.22	5.45	8.67	843	12.89
5	3.22	5.04	8.24	1002	11.85
6	3.95	4.43	8.38	946	12.35
7	3.22	5.04	8.26	998	11.58
8	3.22	5.24	8.46	900	13.41
9	3.95	6.37	10.32	858	11.50
10	3.22	5.86	9.08	955	13.32
11	3.95	6.37	10.32	920	13.00
12	3.95	5.09	9.04	796	11.96
13	3.22	5.45	8.67	926	11.70
14	3.95	6.37	10.32	955	12.22
15	3.95	6.37	10.32	954	14.28
16	3.95	5.09	9.04	936	13.00
17	3.95	5.26	9.21	1021	11.10
18	3.95	6.37	10.32	656	1150
19	3.22	5.86	9.08	1110	11.24
20	3.22	5.04	8.26		12.36
21	3.22	5.45	8.67	1021	11.24
Average	3.76	5.51	9.19	999	12.21

TABLE IV

Body (4)

1	3.73	2.28	6.01	488	19.50
2	3.73	2.49	6.22	534	18.40
3	4.16	2.50	6.66		18.30
4	3.73	2.91	6.64		18.80
5	4.16	2.96	7.12	635	18.60
6	4.16	2.50	6.66		18.10
Average	3.97	2.60	6.55	552	18.60

TABLE V

Body (5)

Member	Percent Drying Shrinkage	Percent Fire Shrinkage	Percent Total Shrinkage	Modulus of Rupture #/sq. in.	Percent Absorption
1	5.26	5.26	10.52	1138	14.29
2	4.61	5.24	9.85	940	14.03
Average	4.93	5.25	10.18	1039	14.16

Note: In the modulus of rupture calculations any variations above 15% from the average was thrown out, and the average recalculated.

DISCUSSION OF DATA

Table I.

Body (1) b, using floated barite had a fair modulus of rupture (378# per square inch). The shrinkage was moderate (total shrinkage was 6.52%). The absorption was 18.7%, which was somewhat high.

Body (1)a, using crude barite, was inferior to (1) b. It had an absorption of 19.1%, and a modulus of rupture of 274# per square inch, which was lower than that of (1) b. The total shrinkage was somewhat higher than in body (1) b, 6.62%, as compared with 6.52% for (1) b. In both bodies hairline cracks were observed.

Table II.

Body (2) a had an absorption of 18.1%, which is somewhat high. The modulus of rupture (443# per square inch), is fair. The shrinkage was moderate, total shrinkage being 6.47%.

Body (2) b had a lower modulus of rupture (331# per square inch). The absorption, 17.0%, is lower. The total shrinkage, 5.54%, is lower than in (2) a. Hairline cracks were observed in both bodies.

Table III.

This body was very good. The modulus of rupture was 999# per square inch. The absorption, 12.21%, was much lower than any of the above bodies. The total shrinkage was 9.19%, which was moderate. Hairline cracks were observed.

Table IV.

This body had a modulus of rupture of 552# per square inch, which is fairly good. Absorption, which is 18.7%, is rather high. Total shrinkage was 6.55%, which is good. Hairline cracks were also observed in this body.

Table V.

This was a very good body. The modulus of rupture was 1039. Absorption was lower than all the others except body No. 3. The total shrinkage, 10.18%, was higher than in the other bodies, but was not excessive. A few hairline cracks were observed, but this was not as bad as in the others.

CONCLUSIONS

From the results of this investigation the following conclusions were drawn:

1. Barite can be successfully substituted for barium carbonate in a whiteware body suitable for the manufacture of white brick.

2. Sandy kaolin can be used to furnish part of the silica and replace some of the plastic Georgia kaolin. It should be ground to pass 20-30 mesh.

3. South Carolina silica can be successfully employed in making a good white brick. This was the best body of all those investigated, as far as modulus of rupture and texture goes.

4. Ottawa sand is not as good as potters flint or South Carolina silica in a body. In fitting, the sand does not have intimate enough contact with the other ingredients.

5. Finer grinding of the frit will give a stronger body.

6. Crude barite in a body does not noticeably affect the color of the body.

RECOMMENDATIONS FOR FURTHER RESEARCH

For further research it would be advisable to investigate further into the possibilities of South Caroline silica and its use in raw and fritted bodies of the nature of those investigated in this research.

The best size which silica should be ground for incorporation into a frit, and into the body should be investigated, and the effect of gradation of grain sizes on the strength of the body.

The effect of aging the body before the forming operation in order to uniformly distribute the water content throughout the mass should be investigated.

The best method of forming the brick should be investigated, with a view to securing the lowest porosity and greatest strength.

A comparative study might be made of the effect of crude barite and floated barite.

Research is advisable as to the use of barite as an auxiliary flux in other whiteware bodies.

APPLICATION TO INDUSTRY

While the scope of this research was necessarily limited to white building brick, it is quite possible that barite can also be used as an auxiliary flux in other whiteware bodies.

There is still a good market for white brick in the southern trade, and in the writer's opinion a profitable business could be established along this line.

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Trans. Amer. Ceram. Soc., Vol. XIX, p. 457

Stull — Beneficiation and Utilization of Georgia Clays
U.S.B.M. Bulletin 252

Waldschmidt — Fusion Study of High Feldspar Area in Feldspar - Kaolin - Quartz System
Jour. Amer. Ceram. Soc., 16, 4 (1933), p. 199-203

ABSTRACTS

Auxiliary Fluxes in Ceramic Bodies

By Paul F. Collins, Jour. Amer. Cer. Soc., 15, 1, 1932

The fluxes investigated were of the simplest type. They were chosen from low temperature mixtures of alkalies or alkaline earths and SiO_2 or B_2O_3, and between alkalies or alkaline earths and SiO_2, B_2O_3 or Al_2O_3.

The results of this experiment strongly indicate that the auxiliary glass serves as the primary vitrifying agent or solvent and that the feldspar only serves as a source for further glass development in the final stages.

Utilization of Feldspar - Alkaline Earths as Vitrifying Agents for Georgia Kaolin

Thesis by C. M. Dodd, O.S.U

(1927)

Georgia Kaolin vitrifies at cone 30 unless flux is present. Feldspar is suitable but auxiliary flux is necessary to lower the vitrification temperature to a commercially practicable temperature.

1. A binary system, A, of twenty-one members, with feldspar and BaO as end members was developed. The eutectic point was found at A_8. This composition was 39.7% $BaCO_3$ and 60.3% commercial potash spar.

2. A ternary system, B, with three eutectic compositions, orthoclase, calcite, orthoclase magnesite, and A_8 as end members The eutectic composition B_n was found.

3. Member B_n, Georgia Kaolin and flint were taken as end members in series C.

In the ternary system $BaCO_3$, $CaCO_3$ and feldspar, the eutectic was found to be 33% $BaCO_3$, 11.4% $CaCO_3$, 55.5% potash spar at cone 05.

In Body C_2, composed of 10% $2B_8$, 40% flint and 50% Georgia Kaolin, absorption was 11.27%, color was good, and Modulus of Rupture was high.

The composition of approximately 6.66% spar, less than .25% $MgCO_3$, about 1% $CaCO_3$, less than 2% $BaCO_3$, 50% Georgia Kaolin, and 40% flint was the best and was recommended for use for building brick.

Barite and Barium Products

By R. M. Santmyers and B. H. Stoddard

Mineral Resources of U.S., (1930), p. 291-301

The mine production of crude barite in the United States in 1930 was 237,505 short tons, of which Missouri produced 139,889, or 59% of the total. Other important barite producing states are Georgia, California, Tennessee and Virginia. The average value per ton in 1930 was $6.67 per long ton.

Apparent stocks on hand at mines at the end of December, 1930 were about 44,200 short ton, of which 1500 tons were held in Georgia, 37,700 tons in Missouri, and 5,000 tons in Nevada.

Refined ground barite sold in 1930 amounted to 55,284 short tons, valued at $1,140,305. The average value was quoted at $18.00 per long ton in Georgia, and $23.00 per short ton in Missouri.

The crude barite contained 95% $BaSO_4$, and less than 1% of iron, being quoted at 7 - 8 dollars per ton.

Barium carbonate was quoted at $47.00 per ton in 1930, which is about six to seven times the cost of crude barite.

A Deformation Study of BaO, Al_2O_3, SiO_2 mixtures

By A. S. Watts - Trans. Amer. Ceram.

Soc., Vol XIX, p. 457

A series of mixtures was compounded of $BaCO_3$, kaolin, and flint. The Al_2O_3 was contained in the kaolin.

Rate of heat increase was 75° C. per hour for fifteen hours, then 40° C. per hour till deformation started, and then 20° C. per hour.

The eutectic found was either 35% BaO, 10% Al_2O_3, and 55% SiO_2, or 40% BaO, 10% Al_2O_3, 50% SiO_2. Both deformed completely at cone 6 down.

Fusion Study of High Feldspar Area in Feldspar - Kaolin - Quartz System

By M. H. Waldschmidt -

Jour. Amer. Ceram. Soc., 16, 4 (1933)

The system was divided into four equal parts:

(A) 50% or more feldspar, 50% or less kaolin, 50% or less quartz.

(B) Less than 50% of any of the three

(C) More than 50% quartz, less than 50% feldspar, less than 50% kaolin

(D) More than 50 % kaolin, less than 50% feldspar, less than 50% quartz.

Part A was studied first, as the glassy phase is located in this area.

Conclusions.

1. Deformation of the ternary eutectic was found to be 92.5% feldspar, 5% kaolin, and 2.5% quartz.

2. Deformation of the binary eutectic between feldspar and quartz was 95% spar, 5% quartz.

3. Deformation of the binary eutectic between feldspar and kaolin was 92% spar, and 8% kaolin.

Beneficiation and Utilization of Georgia Clays

By R. T. Stull and G. A. Bole, U.S.B.M.

Bulletin 252

Samples were taken from mines and undeveloped deposits. It was found:

1. That Georgia contains a large area of sedimentary kaolins and bauxites of importance.

2. Georgia clays can be washed free from material that causes dark specks in the ware; by proper blending a uniform product can be marketed.

3. The working properties and fire tests of most of the crude clays are from fair to good.

4. High bisque losses and shrinkage can be overcome by proper body mixes.

5. There are large deposits of high grade refractory clays, for grog brick.

6. Light cream and light gray face brick can be made from a mixture of Georgia kaolin, apatite, and sand.