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CONTROL OF IRON OXIDE IN VOLCANIC ASH

By

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Object. One of the potential uses of volcanic ash is that of a component in glazing mixtures for the ceramic industry. For this it is well suited, except for the small amount of iron oxide present which is sufficient to impart a bluish green coloration to the finished article. Our object was to eliminate the influence of iron, either by its removal, or through other means.

Results. Mechanical concentration, magnetic concentration and leaching were all found unsuccessful. Finally, using reagents in the melt, and by this means producing colors which would act in a complementary manner with the blue green of the iron, very satisfactory results were obtained. Glazes containing suitable amounts of ash which are colorless, or in some cases almost colorless, can be produced with practically no extra cost.

The following are results of the investigation:

Volcanic Ash
Table I
Chemical Composition

	Sample 1 McPherson Co.	Sample 2 Lincoln Co.	Sample 3 Meade Co.
	Per cent	Per cent	Per cent
Ignition loss	5.00	4.60	4.60
Alkalies Na_2O+K_2O	4.70	5.64	4.82
CaO	0.70	1.00	1.68
MGO	0.30	0.21	0.13
Al_2O_3	14.15	14.46	10.65
Fe_2O_3	1.65	1.54	2.65
SiO_2	72.50	73.30	72.40
Total	99.00	100.75	96.93

The ignition loss on samples 1 and 2 represents occluded water and ordinary moisture. (On No. 1, the moisture is 0.99%). The ignition loss on sample 3, represents occluded water, moisture, and an undetermined amount of carbon dioxide. The latter indicates some of the lime is present as carbonate, probably of secondary origin.

Some Physical Properties

Sample 1, McPherson County volcanic ash, was used in these tests. It is light gray in color and consists of an almost uniform mixture of finely divided particles of rock glass. Rock glass is a solid solution of silicates. Also present are loosely coherent concretions, of almost the same composition, and, using the microscope, a few widely scattered grains of feldspar can be observed. The percentage of the latter is very small. See figure I.

Fig. I
Volcanic Ash
Natural Size

Table II compares the analysis of the ash and concretions.

Table II

	SiO_2 Per cent	Fe_2O_3 %	Al_2O_3 %	CaO %	MgO %	K_2O Na_2O %	Loss on Ignition %	Total %
Ash	72.50	1.65	14.15	0.70	0.30	4.70	5.00	99.00
Concretions	70.50	2.13	13.67	0.68	0.31	6.71	5.00	99.00

Probably 50% of the ash will pass through a 200 mesh screen and 20% through a 300.

For a detailed discussion of the physical properties, see "Volcanic Ash Resources of Kansas".[1]

Water Concentration

The ash being a uniform mixture of complex particles of practically identical composition, the removal of any constituent, like iron oxide, by mechanical concentration, offers little inducement. This is shown in the following carefully conducted panning test:

Original sample	400 grams
Concentrate	11.23 "
Tailings	388.77 "

The analyses are:

Table III

	Original %	Concentrate %	Tailings %
Ignition Loss	5.00	5.00	5.00
$Na_2O + K_2O$	4.70	5.98	4.64
CaO	0.70	0.80	0.60
MgO	0.30	0.30	0.30
Al_2O_3	14.15	13.00	14.20
Fe_2O_3	1.65	1.54	1.70
SiO_2	72.50	72.40	73.00
Total	99.00	99.02	99.44

Magnetic Concentration

No particles in the ash showed any traces of magnetism either roasted or unroasted. Roasting under oxidizing conditions changes the color of the ash from gray to red, due to oxidation of the ferrous iron. Under reducing conditions there is no change.

Centrifugal Classification

A sample of the ash was sent to the Federal Pneumatic Systems, Inc., of Chicago, by Mr. Norman Plummer[2], for testing. In this system classification is effected by opposing one centrifugal current of air to another. The results showed no separation of the chemical constituents could be made, but the test is interesting in showing how volcanic ash can be classified according to grain size. Their report follows.

Table IV
500 grams to test

1642	5/8" orifice	fines 22.5 grams (estimated by writer at -300 mesh)
1643		rejects 465.0 grams, balance of ash.
	440.1 grams to test for rejects.	
1644	3/4" orifice	fines 21.3 grams (estimated-250 mesh)
1645	3/4" "	rejects 411.2 grams, balance of ash.
	437.5 grams to test for rejects.	
1646	1" orifice	fines 164.7 grams (estimated-200 mesh)
1647		rejects 216.5 grams, balance of ash.

Analysis of different sizes from above test

Table V

No.	SiO_2 %	Fe_2O_3 %	Al_2O_3 %	CaO %	MgO %
1642	70.6	1.42	13.48	2.20*	0.30
1643	72.1	1.50	13.50	0.73	0.31
1644	74.6	1.50	13.10	1.10	0.31
1645	73.3	1.57	13.40	0.66	0.33
1646	73.7	1.50	13.70	0.86	0.34
1647	71.7	1.57	13.83	0.68	0.31

* Salted in testing.

Leaching Tests.

Leaching results were unsatisfactory. Generally speaking, neither the ash itself, or much of the iron present, is soluble in acids or dilute alkalies, either hot or cold. Repeated tests with 10% sulphuric acid gave only a 13% extraction of iron oxide. This small amount of iron is probably from oxide coatings deposited by the infiltration of ferruginous waters. Apparently the iron as silicate is not affected.

The Use of Decolorizing Agents, or Complementary Colors.

Four different glazing mixtures were tested containing 5.18%, 10%, 15%, and 20% of volcanic ash, respectively. Using a gas furnace, fifty gram lots of the mixtures were melted in fire clay crucibles and poured on a flat iron plate for observation.

The composition of the 5.18% ash mixture was:

Flint sand	61.81	per cent
Volcanic ash	5.18	" "
Soda ash	28.10	" "
Whiting ($CaCo_3$)	4.91	" "
	100.00	" "

Table VI - 5.18% Volcanic Ash.

No.	Selenium	Manganese Dioxide	Nickel Oxide	Cuprous Oxide	Color
	%	%	%	%	
14					Pale bluish green
15	0.001				Colorless (best)
16	0.002				Slightly brown
17		0.002			Very slight green
18			0.002		Pale bluish green
21			0.004		Pale grayish green

The selenium in these tests was used under reducing conditions.

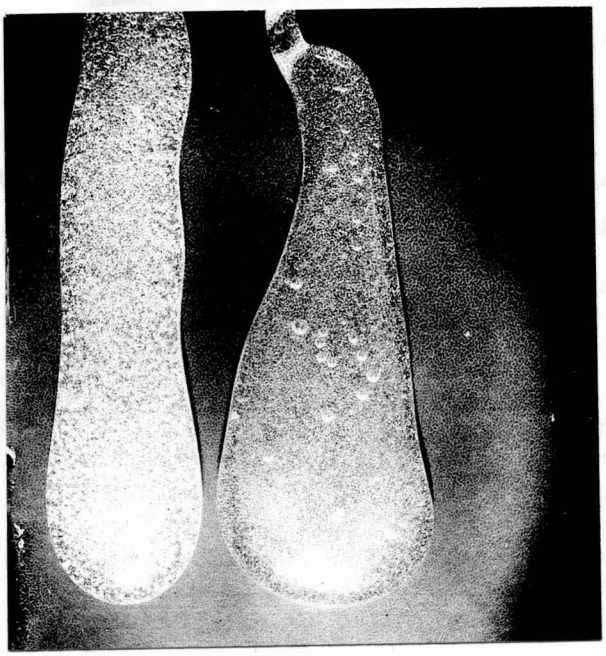

Fig. 2.
Natural Size

Sample 14
Volcanic ash 5.18%

Sample 15
Volcanic ash 5.18%
Selenium 0.001%

The composition of the 10% ash mixture was:

Flint Sand	50%
Volcanic ash	10%
Soda ash	30%
Whiting	5%
Borax glass	5%
	100%

Table VII - 10% Volcanic Ash.

No.	Selenium	Manganese Dioxide	Nickel Oxide	Arsenic Trioxide	Cobaltic Oxide	Cuprous Oxide	Potass. Permanganate	Color
	Per cent							
29								Greenish blue
30	0.002							Greenish brown
31	0.004							Distinct brown
32		0.002						Bluish green
33		0.004						Bluish green
34			0.002					Bluish green
35			0.004					Gray green
36	0.001							Brownish green
37	0.0015							Brownish green
38	0.002			0.02				Faint greenish gr
39	0.0015			0.02				Faint green
40					0.002			Bright blue
41						0.002		Bluish green
42	0.0015			0.04				Grayish green
43	0.002			0.04				Faint grayish gree
44			0.003					Greenish blue
45						0.003		Bluish green
46					0.003			Bright blue
47							0.003	Light bluish gree
48			0.005					Grayish green
49	0.001			0.02				Light green
50	0.001			0.04				Very faint green-ish gray (best)

The composition of the 10% ash mixture was:

Flint Sand	50%
Volcanic ash	10%
Soda ash	30%
Whiting	5%
Borax glass	5%
	100%

Table VII - 10% Volcanic Ash.

No.	Selenium	Manganese Dioxide	Nickel Oxide	Arsenic Trioxide	Cobaltic Oxide	Cuprous Oxide	Potass. Permanganate	Color
	Per cent							
29								Greenish blue
30	0.002							Greenish brown
31	0.004							Distinct brown
32		0.002						Bluish green
33		0.004						Bluish green
34			0.002					Bluish green
35			0.004					Gray green
36	0.001							Brownish green
37	0.0015							Brownish green
38	0.002			0.02				Faint greenish gray
39	0.0015			0.02				Faint green
40					0.002			Bright blue
41						0.002		Bluish green
42	0.0015			0.04				Grayish green
43	0.002			0.04				Faint grayish green
44			0.003					Greenish blue
45						0.003		Bluish green
46					0.003			Bright blue
47							0.003	Light bluish green
48			0.005					Grayish green
49	0.001			0.02				Light green
50	0.001			0.04				Very faint greenish gray (best)

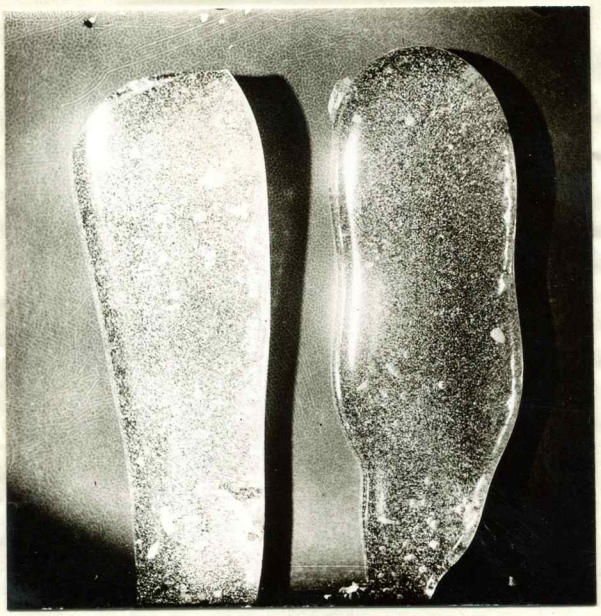

Fig. 3
Natural Size

Sample 29
Volcanic ash 10%

Sample 50
Volcanic ash 10%
Selenium 0.001%
Arsenic trioxide 0.04%

The composition of the 15% mixture was:

Flint sand	45 %
Volcanic ash	15 %
Soda ash	30 %
Whiting	5 %
Borax glass	5 %
	100 %

Table VIII - 15% Volcanic Ash.

No.	Selenium %	Arsenic Trioxide %	Color
51			Bright greenish blue
52	0.0015		Light brownish green
53	0.0015	0.08	Light greenish gray
54	0.003		Brownish green
55	0.003	0.08	Light gray green
66	0.003	0.12	Pale grayish green (best)

The composition of the 20% mixture was:

Flint sand	40 %
Volcanic ash	20 %
Soda ash	30 %
Whiting	5 %
Borax glass	5 %
	100 %

Table IX - 20% Volcanic Ash.

No.	Selenium %	Arsenic Trioxide %	Color
56			Strong greenish blue
57	0.004	0.16	Gray green
58	0.0045	0.20	Light brownish green
59	0.0045	0.25	Grayish green
60	0.0050	0.30	Light grayish green
61	0.0045	0.30	Light pale green
62	0.0055	0.30	Light grayish green
63	0.0043	0.220	Grayish green
64	0.0045	0.225	Pale grayish green (best)
65	0.0043	0.200	Grayish green

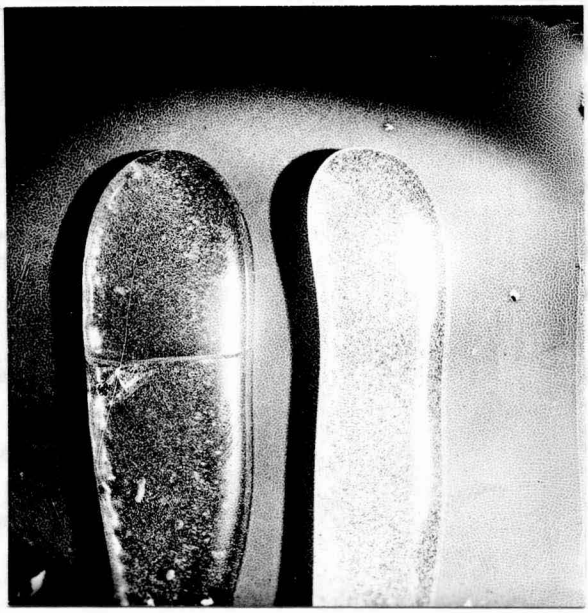

Fig. 4
Natural Size

Sample 56
Volcanic ash 20%

Sample 64
Volcanic ash 20%
Selenium 0.0045%
Arsenic trioxide 0.225%

The color intensity is somewhat dependent on the thickness of the glaze. The samples tested were at least one fourth inch in thickness. Results would be even better in commercial practice where a much thinner coating is employed.

Summary of Different Decolorizers

In these tests, selenium alone, for very small amounts of iron, and selenium and arsenic trioxide, for larger amounts, proved by far the most effective. The amount of iron oxide (in terms of Fe_2O_3) ranged from 0.085% in the low volcanic ash glaze to 0.33% in the highest. This includes iron from the ash only. No doubt there were small amounts from the other substances present.

Selenium. Metallic selenium is used under reducing conditions. It produces a pink glass; due it is said, to colloidal dispersion. Pink is complementary to green. In these tests a slight excess would result in a brown color. Best results were obtained when enough was used to give a faint brown, and then forty or fifty times the weight of selenium in arsenic trioxide was also added.

Arsenic trioxide. This tended to eliminate the brown color due to the necessary selenium. An excess would cause green to reappear. Forty to fifty times the selenium seems the correct amount. This oxide is said to keep selenium from oxidizing.

Manganese dioxide and Potassium Permanganate. They tend to produce reddish purple shades. With small amounts of iron their use is beneficial. A faint green melt is produced. With more iron the effects are not satisfactory.

Cuprous oxide. No beneficial effects. Decreases the green; increases the blue.

Cobaltic oxide. Produces a bright blue. No improvement.

Nickel oxide (Ni_2O_3). Does some good by substituting a grayish green for greenish blue.

Little time was devoted to a consideration of other possible deoxidizers. The literature on the subject seems limited. This field probably offers good opportunity for research.

The Cost of Decolorizers

The wholesale cost (spring, 1939) of selenium is $1.75 per pound; arsenic trioxide $0.03 per pound. The cost of decolorizing one ton of a 10% volcanic ash glaze with the amounts of these substances required, as indicated in this report, would be about six cents.

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