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PROJECT 1/1/5

LIGHTWEIGHT AGGREGATE

Laboratory Testing of Clays and Shales

by

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1. INTRODUCTION

In 1959 Hosking and Sheridan, at the request of the South Australian Government Department of Mines, examined the use of fine mica as an additive to clays in order to promote bloating for the production of lightweight aggregate. They tested 18 clays, none of which bloated appreciably on firing to 1340°C, and found that mica additions did not improve the bloating properties significantly. They recommended that no further work on the addition of mica be undertaken, but suggested that a search be made for naturally bloating clays and shales. The Department of Mines took up this suggestion, and 84 samples were submitted for preliminary testing (Olliver, 1961). This survey revealed a number of potential bloating materials, and 15 samples were selected for more detailed examination, the results of which are given in the present report.

2. SUMMARY

The results of firing tests made on 11 samples of shale and 4 samples of clay in oxidising and reducing atmospheres for various heating times over an extended temperature range are reported. The bloating index, a quantitative measure for the comparison of bloating materials, is described. The introduction contains a critical review of the literature on the causes of bloating. Three shale samples (A3342/61, A3344/61 and A3346/61) and one clay sample (A3458/61) are recommended for pilot tests in a rotary kiln.

3. THE CAUSES OF BLOATING

For bloating to take place some mineral or combination of minerals must be present that will dissociate to liberate a gas at the time when the mass of the clay or shale has fused to a melt sufficiently viscous to prevent the escape of the gas.

Riley (1951) examined the limits in the proportions of silica, alumina, and total fluxing agents beyond which the mass of the clay either will not fuse at a temperature low enough, or will fuse to a melt not viscous enough, to trap the gas. He defined an "area of bloating" within which the chemical composition of a clay must fall if it is to bloat. It does not however follow that a clay will bloat if its composition falls within the bloating area, since a constituent capable of producing a gas at the proper temperature may be lacking. A more detailed summary of this work is given in the report of Hosking and Sheridan (1960).

From tests made with synthetic mixtures Riley concluded that pyrite, haematite, dolomite and possibly calcite can produce a gas at a temperature high enough to cause the bloating of a clay. Since the dissociation of pyrite to pyrrhotite takes place at too low a temperature to be a likely cause of bloating, he suggested a second reaction, the oxidation of pyrrhotite to sulphur dioxide:

$$2\ FeS + 3O_2 = 2\ FeO + 2SO_2$$

Dolomite produced an excellent bloat when added to non-bloating mixtures. Dolomite dissociates in 2 stages: CO_2 equivalent to the MgO content of the dolomite is liberated at about 750°C and above 770°C only periclase and calcite remain. Calcite rapidly decomposes above 890°C. Since the dissociation of dolomite cannot continue to a temperature high enough to cause bloating, Riley supposed that intermediate compounds must be formed at a lower temperature which are able to retain some at least of the carbon dioxide and dissociate near 1200°C.

Calcite caused a very poor bloat, partly because of its good fluxing properties: it produced a melt of so low a viscosity that any gas liberated would probably escape. As with dolomite, the formation of intermediate compounds was postulated to explain the presence of gas at temperatures as high as 1200°C.

One of the first theories of bloating was that of Jackson (1903), who attributed the bloating of clays to the evolution of oxygen liberated during the dissociation of ferric oxide contained in the clay. Jackson's theory was supported by Riley, who considered that the dissociation of ferric oxide was an important factor in the bloating of clays. Thermodynamic data for the reactions

$$3Fe_2O_3 = 2Fe_3O_4 + \tfrac{1}{2} O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$Fe_3O_4 = 3FeO + \tfrac{1}{2} O_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2),$$

taken from Kubaschewski and Evans (1958), are as follows:

Reaction	Free energy charge, ΔF (Cal.)	Temperature Range, °K
1	59,620 - 33.62 T	298 - 1460
2	74,620 - 29.9 T	298 - 1642

The equilibrium constant K for each reaction is given by the relation

$$\log K = \frac{-\Delta F}{4.576\ T}$$

where ΔF is the free energy change and T the absolute temperature, and the dissociation pressure of oxygen in atmospheres is equal to K^2. From these relations the figures given in Table 1 have been calculated.

TABLE 1: DISSOCIATION OF HAEMATITE AND MAGNETITE

Reaction	Temp °C	ΔF k. cal.	Dissociation Pressure mm Hg
$3Fe_2O_3 = 2Fe_3O_4 + \tfrac{1}{2}O_2$	1000	16.8	0.0013
	1100	13.5	0.04
	1200	10.1	0.78
	(1300	6.7	10.3)*
$Fe_3O_4 = 3FeO + \tfrac{1}{2}O_2$	1000	36.5	2.4×10^{-10}
	1100	33.6	1.7×10^{-8}
	1200	30.6	6.8×10^{-7}
	1300	27.6	1.7×10^{-5}

* extrapoloated.

Since the expansion must take place against atmospheric pressure, it seems unlikely, in view of these results, that the dissociation of ferric oxide, and much less of magnetite, can play a significant part in the bloating of clays and shales.

Ehlers (1958) examined a number of clays and shales that showed excellent bloating characteristics and determined the gases present in the ~~residues~~ vesicles of the bloated material by gas chromatography. Of 6 samples examined, 5 showed the entrapped gases to be entirely CO_2 and one showed almost all CO_2, with a slight trace of SO_2. The source of CO_2 was not organic matter, since treatment of the samples with hydrogen peroxide to destroy organic matter did not affect the bloating characteristics. Four of the samples contained calcite and the other two ankerite, $Ca(Fe, Mg)(CO_3)_2$. Treatment of the samples with hydrochloric acid to decompose carbonate entirely destroyed the bloating effect, and Ehlers concluded that the carbonate minerals were the cause of bloating.

Ankerite decomposes in two stages, half the CO_2 being given off at 690°C and the other half at 898°C, the decomposition temperature of calcite. It would therefore seem that most of the CO_2 should be lost before the bloating temperature, which is usually in the range 1100-1300°C, is reached. If equilibrium conditions prevailed, this would be so, and Ehlers found that preheating the samples for an hour at 926°C destroyed the bloating properties. He also found that the temperatures at which the bloating gases were lost during prolonged low temperature firing were in general much lower then the decomposition temperatures of the carbonate minerals in question. This may be explained by the presence of other phases, and it is known, for example, that in the presence of quartz calcite may give off CO_2 at temperatures as low as 400°C.

Ehlers rejected Riley's suggestion that the CO_2 which leaves the carbonate mineral might be recombined into a phase which is stable into the bloating range, such as potassium carbonate or a member of the cancrinite group, for several reasons, of which the most cogent is that if the heating rate is slow, the amount of bloating is decreased, although there should be a greater chance for mineral recombinations to take place, and hence more CO_2 preserved for bloating at high temperatures. He believes that CO_2 is retained within the sample as a result of non-equilibrium conditions that prevail with flash heating. Rapid heating of the exposed surface of a sample causes the formation of a viscous skin before the inner part has reached a high temperature. As heating proceeds, carbonate in the inner part of the samples decomposes and CO_2 is trapped within the glassy surface layer. Support for this theory was found in the observation that in some samples examined the greatest cellular development was around the outer edge rather than evenly distributed throughout the sample. Recombination of the carbonate to form a mineral stable into the fusion range should give an even distribution of vesicles rather than a structure of this type.

Everhart (1959) reported the results of the examination of 96 samples of clays and shales, of which 18 were found to be non-bloating. In the 78 bloating samples the average ratio of illite to kaolinite was 2.7, in the non-bloating samples the ratio was 1.6. Since illites fuse between 1000 and 1300°C and kaolinites between 1650 and 1780°C, he considered that proper viscosity conditions in the melt could be achieved by the presence of a suitable proportion of illite. Two gases were found in the vesicles of the bloated samples, CO_2 and SO_2, but in no case was SO_2 found as the sole bloating agent. Water vapour, proposed by some investigators, was never found as a primary cause of bloating, and this is confirmed by the work of Hosking and Sheridan (1960), who were unable to achieve bloating by the addition of mica to non-bloating materials. Each of the bloating samples contained either calcite, dolomite or ankerite, usually calcite. Siderite was present in several, but always in the presence of one of the other carbonate minerals, and in no case was it established as the sole source of CO_2. Everhart concluded from these results that material suitable for bloating will contain a high proportion of illite and one of the carbonate minerals calcite, dolomite or ankerite, and that an X-ray examination will serve to separate the potentially promising samples from those of no promise.

Most of the work reported by Everhart was carried out by Ehlers, and their joint thesis finds some support in the earlier work of Conley and his associates (1948). They tested 81 clays, of which 39 were considered bloaters. The average pH of the bloating clays was 6.6, of the non-bloaters 4.4. Most of the bloating clays had values above 5, and most of the non-bloaters below 5. There were exceptions both ways, amounting to about 10 per cent of the total. Their laboratory testing included two separate heat treatments, a slow heating, from room temperature to the bloating temperature in about 2 hours, and a flash heat treatment. Most naturally bloating clays showed some signs of bloating during the slow run, but usually considerably more when given the flash-heat treatment. Many clays that bloated very well under the flash-heat treatment showed no indications of bloating during the slow run. These observations are in accord with the theory that bloating is caused by carbonates, particularly calcite, but not with the theory that it is caused by ferric oxide.

Hill and Crook (1960) have returned to the original theory of Jackson (1903), that bloating is caused by the dissociation of ferric oxide. They concluded that in the samples they examined the most common gas-producing reaction was the reduction of iron oxide to the ferrous state, and that the evolution of CO_2 from carbonates was not important. Also that elemental sulphur derived from the reaction of ferrous sulphide with oxygen was a cause of bloating. They set the requirements for good bloating at from 3 to 10 per cent of alkaline earth oxides and from 5 to 15 per cent of iron oxide.

Their paper gives chemical analyses of the raw materials, showing total CO_2 and total iron, but not ferric oxide, (although the results are expressed as Fe_2O_3). However, a series of samples was fired in a rotary kiln at 3 temperatures, one just below, one in the middle, and a third at the top of the range of bloating temperatures. The ferrous iron was determined in these samples after firing, and the results show that a high proportion of the iron was in a ferrous state when the bloating temperature was reached. Since samples must be regarded as satisfactorily bloated at the middle of the bloating range, the total amount of oxygen available for bloating can be calculated from the difference between the ferrous iron content just before the beginning of bloating and the ferrous iron content at the middle of the bloating range, on the assumption that the increase in ferrous iron is wholly due to the reaction.

$$Fe_2O_3 = 2FeO + \tfrac{1}{2}\, O_2$$

The results of the calculation are shown in Table 2.

TABLE 2: GASES AVAILABLE FOR BLOATING (ml/100 g SAMPLE)

Sample No.	Volume of O_2 at 1150°C	Volume of CO_2 at 1150°C
1	31	558
5	47	313
7	188	-
11	235	876
16	1672	396
17	559	-
18	Nil	7844

If the specific gravity of the raw material is taken as 2.6, 60 ml of gas per 100 g of sample are required at the bloating temperature to cause bloating to a specific gravity of 1.0, provided that none of the gas escapes. It can hardly be doubted that some of the gas will escape, and it is therefore very likely that considerably more than 60 ml per 100 g of sample will be required. In any case, there is insufficient oxygen to bloat Nos. 1 and 5. The authors attribute the bloating of No. 18 to the presence of pyrite.

The thermodynamic data show that ferric oxide will not dissociate to ferrous oxide at bloating temperatures (Table 1), though the possibility of reaction with other minerals is not ruled out. If dissociation were to proceed only to the stage of magnetite, the amount of oxygen produced would be only one third of that shown in Table 2. In every case where the analysis is given there is adequate CO_2 to account for the bloating.

It must be concluded from the above discussion that the results reported by Hill and Crook are not adequate to prove their conclusion that liberation of oxygen from ferric oxide was the cause of bloating. The cause or causes of bloating must still be considered uncertain. While oxygen may play a part, the weight of evidence supports the view that carbon dioxide derived from carbonate minerals is the principal bloating agent. Because of these uncertainties it was not possible to rely on chemical or petrological examination for diagnostic purposes, and all the samples were submitted to firing tests.

4. MATERIAL EXAMINED

The samples examined are listed in Table 3.

TABLE 3: DESCRIPTION OF SAMPLES

Sample No.	Material	Section	Hundred	Locality
A 3341/61	Shale	487	Noarlunga	Hallets Cove area
A 3342/61	"	566	"	"
A 3343/61	"	563	"	"
A 3344/61	"	79	"	"
A 3345/61	"	124	"	"
A 3346/61	"	1041	Adelaide	Blackwood area
A 3455/61	Clay	104	Yatala	Grange
A 3456/61	"	921	Pt. Adelaide	Wingfield Little Para area
A 3457/61	"	1012	" "	"
A 3458/61	"	3070	" "	"
A 1078/62	Phyllite	895	Noarlunga	Sturt Creek
A 1079/62	Slate	22	"	"
A 1080/62	Shale	1003	Adelaide	Eagle on the Hill, Crafers
A 1081/62	"	969	"	Greenhill Road
A 1082/62	"	1022	"	"

The samples were put through a jaw crusher set at ½ inch and portion of the crushed material was riffled out for screen analysis, results of which are shown in Table 4. The remainder was reduced to minus ½ inch by grinding the over sized particles in rolls, and the fine material was removed by screening on a 10-mesh screen and discarded. The 4 clay samples were sufficiently reduced in the jaw crusher and did not require grinding. One of them, No. A 3458/61, was too wet to be crushed, and was therefore dried by heating for 2 days at 85°C.

TABLE 4: SCREEN ANALYSIS OF CRUSHED SAMPLES

Sample No.	Per cent by Weight					
	+ ½ in.	+ ⅜ in.	+ ¼ in	+ 3/16 in	+ 10 mesh	- 10 mesh
A 3341/61	24.1	47.3	66.1	74.6	88.6	11.4
3342	25.6	43.4	61.1	71.3	88.1	11.9
3343	22.4	46.4	64.6	74.8	89.6	10.4
3344	21.7	51.3	64.9	74.1	87.6	12.4
3345	37.0	59.0	73.8	79.5	90.6	9.4
3346	37.4	55.9	69.3	76.8	89.1	10.9
3455	4.3	22.5	45.3	55.1	73.6	26.4
3456	1.8	10.4	22.7	31.8	56.1	43.9
3457	4.7	21.5	38.8	49.0	71.7	28.3
3458	1.7	10.2	23.6	31.3	57.3	42.7
A 1078/62	29.4	57.6	73.1	81.1	92.1	7.9
1079	36.4	60.1	72.4	80.2	91.8	8.2
1080	25.4	43.9	58.7	66.9	82.4	17.6
1081	25.2	53.5	69.4	78.0	89.6	10.4
1082	23.0	43.6	61.2	69.6	84.1	15.9

A sample of Silurian shale from Victoria which is used commercially for the manufacture of lightweight aggregate was tested with the other samples as a control.

5. EXPERIMENTAL PROCEDURE

5.1 Firing Tests

The samples, prepared as described in Section 4, were freed from moisture by heating for 2½ hours at 180°C. This preliminary heating of the samples was necessary to prevent decrepitation when they were introduced into the high temperature of the electric furnace. The electric muffle furnace used for the firing tests was heated by Globar elements and was fitted with an automatic temperature controller-recorder. About 20 g of moisture-free material were placed on a stainless steel tray which was then introduced into the furnace at the required temperature. Introduction of the sample caused the furnace temperature to drop, and from 1.5 to 2.5 minutes were required for the original temperature to be regained. The residence time of the sample in the furnace was measured not from the time of introduction but from the time when the original temperature was regained. Tests were made both in oxidising and reducing atmospheres. To obtain a reducing atmosphere the bottom of the muffle was covered with a layer of wood charcoal about

2 inches deep. The oxidising atmosphere was the normal atmosphere of the furnace.

5.2 Determination of Specific Gravity

Since a large number of specific gravity determinations had to be made a method was required that would combine speed with accuracy, and a number of methods was examined.

(1) Sink-float tests in liquids of known specific gravity.
The following liquids were used:

						S.G. at 20°C
Ethyl ether						0.71
Acetone						0.79
Acetone	429.4 ml	+	carbon	tetrachloride	70.6 ml	0.90
"	366.9 ml	+	"	"	133.1 ml	1.00
"	304.4 ml	+	"	"	195.6 ml	1.10
"	241.8 ml	+	"	"	258.2 ml	1.20
"	179.4 ml	+	"	"	320.6 ml	1.30
"	116.8 ml	+	"	"	383.2 ml	1.40
Chloroform						1.49
Carbon tetrachloride						1.60

Each particle was tested to find the liquid in which it barely floated, and the results were averaged to find the value for the sample as a whole.

(2) The weighed sample was placed in a glass cylinder having a graduation mark at 60 ml. A glass stopper was placed on top of the sample to prevent the pieces from floating, and water was run in from a burette to the 60 ml mark. The procedure was then repeated with only the glass stopper in the cylinder, and the difference in the burette readings was taken as the volume of the sample. The ratio of weight to volume then gave the specific gravity.

(3) The weighed sample was tipped into a dish of molten paraffin wax kept in an oven at 110-120°C. The contents of the dish were then poured onto a wire mesh supported on a similar dish and the sample was allowed to drain in the oven for about a minute. The sample was then taken from the oven and allowed to cool on filter paper. Finally the volume was determined by titration as in (2).

(4) The weighed sample was dipped in a dispersion containing 0.1 g of Dow Corning high vacuum grease per 100 ml of ethyl ether and dried in a blast of air. The volume was then determined by titration as in (2).

(5) The weighed sample was waxed as in (3) and reweighed. It was then placed in a wire cage and weighed in water. The specific gravity was obtained from the relation

$$\text{Specific gravity} = \frac{A}{B-D+C}$$

Where A = Weight of unwaxed sample in air
B = Weight of waxed sample in air
C = Weight of cage in water
D = Weight of waxed sample and cage in water.

> In order to determine whether the volume had been significantly increased by the wax coating, the waxed samples, after being weighed in water, were placed on filter papers and heated in an oven at 110°C for 3.5 hours. They were then cooled and weighed in air and water as before. Although from 30 to 65 per cent of the wax absorbed was removed by this treatment, the result obtained for the specific gravity remained the same to 3 significant figures.

The results of specific gravity determinations made by these methods on samples that had been subjected to various heat treatments in an oxidising atmosphere are shown in Table 5. The most accurate method is the gravimetric method (5), but it is very time-consuming. The volumetric method with waxed samples (3) gave results that agree closely with the gravimetric results. The same method applied to unwaxed samples (2) gave high results, owing to absorption of water by the sample (since the volume is determined by difference, absorption of water gives a low result for the volume, and hence a high result for the specific gravity). Waxing the sample effectively prevented absorption of water, as was shown by weighing the waxed sample before and after immersion in water. Treatment with silicone grease gave a water repellant surface, but the results were slightly higher than those obtained with waxed samples, indicating a slight absorption of water. The sink-float method (1), is less accurate in principle than the other methods, since the test liquids increase in specific gravity by steps of 0.1, and the average taken for the final result is not a weighted average. These inherent disadvantages are reflected in the results, but the method is nevertheless sufficiently accurate to be useful as a rapid pilot plant or works test.

The volumetric method with waxed samples (3) was adopted, since it combines rapidly with adequate accuracy, and it is the method by which the results given in Section 6 of this report were obtained.

5.3 Water Absorption

For water absorption tests the samples were bloated under oxidising conditions for 10 minutes at the mid-point of the bloating temperature range, weighed, and immersed in distilled water for 48 hours. The samples were then drained and reweighed after removing surface water with absorbent paper. The gain in weight is equal to the water absorbed.

6. RESULTS

The results of the firing tests of clays and shales are given in Tables 6 and 7. The specific gravity of the original samples, prepared as described in Section 4, is shown in Table 8, together with the increase in volume, expressed as a percentage of the original volume, required to produce a specific gravity of 1.3. The water absorption of the bloated samples is given in Table 9.

TABLE 5: SPECIFIC GRAVITY DETERMINATIONS BY VARIOUS METHODS

Sample			Methods Used				
No.	Heating Time min.	Temp	Sink-float	Volumetric (tritation)			Gravimetric
			(1)	(2)*	(3)*	(4)*	(5)*
3341	5	1150	1.4	-	1.24	-	-
"	10	"	1.0	-	0.97	-	-
"	15	"	1.1	-	1.03	-	-
"	5	1200	0.85	-	0.82	-	-
3342	5	1150	1.2	-	1.13	-	-
"	10	"	1.15	-	1.08	-	-
"	15	"	1.25	-	1.21	-	-
"	5	1200	1.0	-	0.93	-	-
3343	5	1150	1.6	-	1.40	-	-
"	10	"	1.45	-	1.30	-	-
"	15	"	1.45	-	1.23	-	-
"	5	1200	1.4	-	1.13	-	-
3341	5	1125	-	1.19	1.12	-	1.12
3342	10	1125	-	1.39	1.30	-	1.29
3343	5	1175	-	1.26	1.18	-	1.19
3458	5	1175	-	0.77	0.73	-	0.74
"	10	"	-	0.96	0.93	-	0.90
3341	15	1125	-	-	1.16	1.20	-
"	5	1175	-	-	0.78	0.81	-
3342	15	1125	-	-	1.21	1.25	-

* (2) Unwaxed sample.
(3) Waxed sample.
(4) Silicone treated sample.
(5) Waxed sample weighed in water.

TABLE 6:

Sample	Atmosphere	Heating Time min.	Bloating Range °C	Specific Gravity at					
				800	820	850	900	925	950
3455	Ox	5	850-	-	1.35	1.28	1.16	1.09	1.08
		10	1115	-	1.41	1.33	1.24	1.15	0.98
		15		-	-	-	1.17	1.12	1.13
	Red	5	940-	1.53	-	1.44	1.41	1.31	1.25
		10	1075	1.71	-	1.44	1.40	1.36	1.21
		15		1.48	-	1.41	1.43	1.33	1.18
3456	Ox	5	1150-	-	-	-	-	-	-
		10	1200	-	-	-	-	-	-
		15		-	-	-	-	-	-
	Red	5	1100-	-	-	-	-	-	-
		10	1150	-	-	-	-	-	-
		15		-	-	-	-	-	-
3457	Ox	5	960-	-	-	-	-	-	1.46
		10	1100	-	-	-	-	-	1.36
		15		-	-	-	-	-	1.28
	Red	5	925-	-	-	-	1.37	1.23	1.15
		10	1085	-	-	-	1.43	1.29	1.21
		15		-	-	-	1.45	1.28	1.17
3458	Ox	5	975-	-	-	-	-	-	1.40
		10	1160	-	-	-	-	-	1.54
		15		-	-	-	-	-	1.43
	Red	5	975-	-	-	-	1.44	-	1.37
		10	1090	-	-	-	1.40	-	1.36
		15		-	-	-	1.51	-	1.38

BLOATING OF CLAYS

Temperature (°C) shown									
975	1000	1025	1050	1075	1100	1125	1150	1175	1200
-	-	0.76	0.90	0.96	0.85	0.56	-	-	-
-	-	0.83	0.92	-	0.80	-	-	-	-
-	-	1.10	0.92	0.88	0.67	-	-	-	-
-	1.25	1.12	1.20	0.64	0.64	-	-	-	-
-	1.23	1.20	1.19	0.71	-	-	-	-	-
-	1.22	1.11	1.05	0.71	-	-	-	-	-
-	-	-	-	-	1.68	1.40	1.06	1.02	1.04
-	-	-	-	-	-	1.34	1.18	1.27	1.01
-	-	-	-	-	1.55	1.54	1.35	1.16	1.07
-	-	-	-	1.58	1.50	1.42	1.23	-	-
-	-	-	-	1.70	1.02	1.28	0.75	-	-
-	-	-	-	1.51	1.03	1.11	-	-	-
1.18	1.04	0.90	0.87	1.00	0.80	0.73	-	-	-
1.07	0.88	0.86	-	0.88	-	-	-	-	-
1.01	0.92	0.87	1.00	0.93	-	-	-	-	-
-	1.26	1.11	-	0.74	0.62	-	-	-	-
-	1.19	1.07	-	0.74	-	-	-	-	-
-	1.15	1.04	-	0.70	-	-	-	-	-
1.25	1.23	-	1.03	-	1.17	1.13	1.07	0.73	-
1.27	1.27	-	1.18	-	1.32	1.05	0.99	0.93	-
1.32	1.17	-	1.04	-	1.23	0.92	1.08	-	-
1.28	-	0.91	-	-	0.71	-	-	-	-
1.17	-	1.00	-	0.98	0.57	-	-	-	-
1.25	-	0.87	-	1.00	-	-	-	-	-

TABLE 7:

Sample No.	Atmosphere	Heating Time min.	Bloating Range °C	Specific Gravity at 1050	1075	1100	1110
3341	Ox	5	1125-	-	-	1.87	-
		10	1175	-	-	1.88	-
		15		-	-	1.50	-
	Red	5	1100-	1.78	-	1.48	-
		10	1125	1.69	-	1.27	-
		15		1.82	-	1.20	-
3342	Ox	5	1125-	-	-	1.78	-
		10	1200	-	-	1.59	-
		15		-	-	1.54	-
	Red	5	1100-	2.05	-	1.45	-
		10	1125	1.93	-	1.34	-
		15		1.79	-	1.11	-
3343	Ox	5	1150-	-	-	2.26	-
		10	1170	-	-	2.18	-
		15		-	-	2.07	-
	Red	5	1130-	2.20	-	2.03	-
		10	1145	2.09	-	1.77	-
		15		2.18	-	1.67	-
		20		-	-	1.60	-
		30		-	-	1.68	-
3344	Ox	5	1075-	1.66	1.27	1.03	-
		10	1175	1.55	1.26	0.78	-
		15		1.49	1.20	0.81	-
	Red	5	1075-	1.79	1.42	1.15	-
		10	1125	1.59	1.25	1.16	-
		15		1.56	1.23	0.77	-
		20		-	1.15	-	-
		30		-	1.17	-	-
3345	Ox	5	1125-	-	-	1.43	-
		10	1150	-	-	1.52	-
		15		-	-	1.35	-
	Red	5	1100-	2.20	2.06	1.37	-
		10	1125	1.07	1.85	1.02	-
		15		2.05	1.78	1.17	-
3346	Ox	5	1150-	-	-	1.82	-
		10	1225	-	-	1.86	-
		15		-	-	1.59	-
	Red	5	1100-	2.10	1.87	1.34	-
		10	1150	1.98	1.71	1.15	-
		15		1.81	1.60	1.15	-

BLOATING OF SHALES

Temperature (°C) shown							
1125	1150	1175	1200	1225	1250	1275	1300
1.12	1.24	0.78	0.82	-	-	-	-
1.30	0.97	-	0.78	-	-	-	-
1.16	1.03	-	-	-	-	-	-
1.00	0.83	-	-	-	-	-	-
0.85	-	-	-	-	-	-	-
0.70	-	-	-	-	-	-	-
1.31	1.13	-	0.93	-	-	-	-
1.30	1.08	-	0.94	-	-	-	-
1.21	1.21	-	0.98	-	-	-	-
1.34	0.94	-	-	-	-	-	-
1.08	0.92	-	-	-	-	-	-
1.18	0.96	-	-	-	-	-	-
-	1.40	1.18	1.13	-	-	-	-
-	1.30	-	1.35	-	-	-	-
-	1.23	-	-	-	-	-	-
1.77	1.24	-	-	-	-	-	-
1.40	1.19	-	-	-	-	-	-
1.55	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-
-	0.70	0.66	0.59	0.66	-	-	-
0.71	-	0.58	0.72	0.62	-	-	-
-	0.62	0.62	-	-	-	-	-
0.94	0.82	-	-	-	-	-	-
0.77	0.60	-	-	-	-	-	-
0.84	-	-	-	-	-	-	-
0.70	-	-	-	-	-	-	-
0.67	-	-	-	-	-	-	-
1.20	0.71	-	-	-	-	-	-
0.94	-	-	-	-	-	-	-
0.93	-	-	-	-	-	-	-
1.32	0.71	-	-	-	-	-	-
1.08	-	-	-	-	-	-	-
0.96	-	-	-	-	-	-	-
1.51	1.38	1.00	0.90	0.85	-	-	-
1.50	1.27	1.04	0.91	-	-	-	-
1.53	1.24	0.96	0.81	-	-	-	-
-	0.98	-	-	-	-	-	-
-	0.94	-	-	-	-	-	-
-	0.94	-	-	-	-	-	-

Contd.

TABLE 7:

Sample No.	Atmosphere	Heating Time min.	Bloating Range °C	Specific Gravity at 1050	1075	1100	1110
1078	Ox	10	1075-	1.45	1.13	0.87	-
			1100				
	Red	10	1075-	1.67	1.28	0.98	-
			1090	-	-	-	-
1079	Ox	10	1075-	1.37	1.20	0.91	-
			1125				
	Red	10	1075-	1.64	1.25	1.01	-
			1115				
1080	Ox	10	1140-	-	-	1.69	-
			1150				
	Red	10	1115-	-	-	1.51	1.45
			1120				
1081	Ox	10	1125-	-	-	1.38	-
			1150				
	Red	10	1100-	-	1.43	1.22	-
			1125				
1082	Ox	5	1150-	-	-	-	-
		10	1200	-	-	1.79	-
		15		-	-	-	-
	Red	10	1125-	-	1.39	1.32	-
			1165				
Silurian Shale	Ox	5	1175-	-	-	1.95	-
		10	1275	-	-	1.76	-
		15		-	-	1.44	-
	Red	5	1125-	2.02	-	1.57	-
		10	1200	-	-	1.49	-
		15		-	-	1.47	-

CONTD.

Temperature (°C) shown							
1125	1150	1175	1200	1225	1250	1275	1300
-	0.86	1.03	1.09	-	-	-	-
-	-	-	-	-	-	-	-
0.82	0.76	0.77	0.79	-	-	-	-
0.92	-	-	-	-	-	-	-
1.43	1.17	1.16	1.18	-	-	-	-
1.26	-	-	-	-	-	-	-
0.91	0.70	0.91	0.86	-	-	-	-
0.91	0.80	-	-	-	-	-	-
-	1.28	-	-	-	-	-	-
1.53	1.27	1.17	1.08	-	-	-	-
-	1.15	-	-	-	-	-	-
1.19	1.00	0.80	-	-	-	-	-
-	1.46	1.14	1.00	0.87	-	0.53	0.66
-	1.48	0.97	0.85	0.86	0.74	-	-
-	1.30	0.97	1.11	-	-	-	-
1.46	1.22	1.02	0.84	-	-	-	-
0.91	1.06	0.95	0.67	-	-	-	-
1.25	1.01	0.79	0.82	-	-	-	-

TABLE 8: SPECIFIC GRAVITY OF ORIGINAL SAMPLES

Sample No.	Specific Gravity	Increase in Volume Required to Produce a Specific Gravity of 1.3 %
3341	2.53	95
3342	2.68	106
3343	2.55	96
3344	2.21	70
3345	2.58	98
3346	2.38	83
3455	1.67	28
3456	1.82	40
3457	1.93	48
3458	1.85	42
1078	2.52	94
1079	2.51	93
1080	2.34	80
1081	2.36	82
1082	2.14	65
Silurian Shale	2.30	77

TABLE 9: WATER ABSORPTION OF BLOATED SAMPLES

Sample No.	Water Absorption %
3341	2.3
3342	1.3
3343	3.2
3344	7.6
3345	5.7
3346	2.4
3455	25.8
3456	7.1
3457	33.0
3458	12.2
1078	4.1
1079	4.6
1080	3.0
1081	3.7
1082	3.8
Silurian Shale	5.8

7. DISCUSSION

7.1 Effect of Heating Time

The average differences in specific gravity produced by increasing the heating time from 5 to 10, from 10 to 15, and from 5 to 15 minutes, are shown in Table 10 at each temperature for which 5 or more results were available. A negative figure means that the specific gravity decreased with increase in heating time, a positive figure, that it increased.

TABLE 10: EFFECT OF HEATING TIME ON SPECIFIC GRAVITY

Time Increment Minutes	Difference in Specific Gravity						
	1050°	1075°	1100°	1125°	1150°	1175°	1200°
			Oxidising Atmosphere				
5 to 10	.	.	-0.05	-0.04	-0.06	+0.04	+0.02
10 to 15	.	.	-0.17	-0.02	+0.01	.	.
5 to 15	.	.	-0.21	-0.06	-0.06	+0.01	+0.06
			Reducing Atmosphere				
5 to 10	-0.11	-0.05	-0.20	-0.27	-0.16	.	.
10 to 15	-0.04	-0.06	-0.09	+0.03	.	.	.
5 to 15	-0.15	-0.11	-0.29	-0.24	.	.	.

Table 10 shows that in oxidising atmosphere there is at first a decrease in specific gravity as the heating time is increased. As the temperature increases this decrease becomes less until finally the specific gravity increases with increase of heating time. The decrease may be explained by non-completion of the bloating reaction; the increase by the escape of gas bubbles from the semi-plastic mass: at sufficiently high temperatures the bloated structure begins to collapse, with reduction in volume and consequent increase in specific gravity. Similar effects were found in a reducing atmosphere, but they were somewhat more marked. This may be explained by the reduction of iron to the ferrous state, in which it fluxes with silica, whereas ferric iron does not. As more iron is reduced, so the mass becomes more plastic or less viscous and is more easily expanded. The reduction of iron will increase with time until all the iron is reduced.

The change in specific gravity when the heating time was increased from 10 to 15 minutes was generally less than the change in passing from 5 to 10 minutes. Since the effect of time was more marked in a reducing atmosphere, several tests were made with heating times of up to 30 minutes in a reducing atmosphere. These showed little change in specific gravity after 15 minutes.

It may be concluded that for the best results the heating time should exceed 5 minutes but that little is gained by prolonging it beyond 10 minutes. For this reason 10 minutes has been taken as the standard time for calculating the bloating index (see Section 7.2), and the last 5 samples were tested with a 10-minute heating time only.

7.2 Bloating Index

A quantitative measure is desirable for the comparison of bloating materials. Such a measure should give due weight to the bloating range, the bloating temperature, and the degree of expansion, and should increase as the bloating characteristics improve. A measure having these properties has been devised and called the bloating index. It is defined as follows:

$$\text{Bloating index} = \frac{R \times 1000}{T \times D}$$

where R = the bloating range, ^{0}C
T = the temperature (^{0}C) at the middle of the bloating range
D = the specific gravity of the bloated material obtained by heating the sample for 10 minutes at the temperature T.

Zetterstrom and Cole (1956) have defined the lower limit of the bloating range as the temperature at which the sample bloats to an average specific gravity of 1.3, and the upper limit as the temperature at which the pieces stick together appreciably, and this definition of the bloating range has been adopted.

As an illustration of the range of values to be expected, the bloating index has been calculated for a series of South Dakota shales from the results of laboratory bloating tests reported by Zetterstrom and Cole:

Sample Number	Bloating Index
107B	204
110B	126
129	111
127	101
132	86
112B	57
131	42
128	36
130	35

The authors did not consider the last three samples suitable for expansion in a rotary kiln. It seems likely that samples having a bloating index of less than about 60 would not be suitable for the manufacture of lightweight aggregate.

The bloating index for all the samples tested, in both reducing and oxidising atmospheres, is given in Table 11. In every case the value is lower in the reducing than in the oxidising atmosphere.

TABLE 11: BLOATING INDEX

Sample No.	Bloating Index	
	Reducing Atmosphere	Oxidising Atmosphere
3341	21	45
3342	19	60
3343	10	13
3344	39	125
3345	21	23
3346	43	65
3455	111	275
3456	35	39
3457	134	158
3458	111	184
1078	14	23
1079	36	50
1080	3	7
1081	21	27
1082	35	36
Silurian Shale	64	95

It should be noted that the bloating index, while it should be a reasonable measure of the bloating property of clays and shales, is not a measure of the suitability of the bloated product for use as a lightweight aggregate. For this purpose water absorption and compressive strength tests are necessary.

7.3 Effect of Furnace Atmosphere

In a reducing atmosphere bloating began at from 0 to 50°C lower than in an oxidising atmosphere, with one exception, No. 3455, for which the position was reversed and bloating began at 90°C higher in the reducing atmosphere. No explanation for this is known, but it should be noted that this sample began to bloat at a temperature lower then that of any other sample, and also that the degree of expansion required to reach a specific gravity of 1.3 was very low, only 28 per cent, so that this sample may be regarded as abnormal. The average difference in temperature between the beginning of bloating in oxidising and reducing atmospheres was 17°C.

The upper limit of bloating in reducing atmosphere was from 10 to 75°C below that in oxidising atmosphere, the average difference being 42°C. The bloating range in reducing atmosphere is thus shorter than the range in oxidising atmosphere by on the average 25°C. There was only one exception to this, the clay sample 3457, which had a bloating range of 140°C inoxidising and 160°C in reducing atmosphere. This sample, like 3455, had a very low lower limit of bloating, and the difference may not be significant: it could be accounted for by experimental error and fluctuation in the composition of the sample.

The lower bloating temperature in reducing atmosphere may be explained by the reduction of iron to the ferrous state, in which it fluxes with silica and so confers greater plasticity on the material. The end of the bloating range is also reached sooner since the production of slag forming compounds by reduction causes the particles to become sticky and to adhere to each other at a lower temperature than they would otherwise do.

The atmosphere in an oil fired rotary kiln working efficiently is likely to be slightly oxidising, or at least neutral, but not reducing. The results of firing tests conducted in an oxidising atmosphere should therefore be preferred to those obtained in a reducing atmosphere. Conversely, since Table 10 shows that better results are obtained in an oxidising atmosphere, care should be taken to see that the fuel supplied to a bloating kiln is completely oxidised in the kiln.

7.4 Water Absorption

There is a very marked difference between the clays and shales. The average water absorption for the clay samples is 19.5, and for the shale samples 4.0. The clay samples, except No. 3456, bloated at lower temperatures than the shale samples. It is perhaps significant that of the clay samples No. 3456 had the lowest moisture absorption (7.1 per cent).

8. CONCLUSIONS

Samples A3343/61, A3345/61, A1078/62, A1080/62 and A1081/62 have a bloating range of less than 50°C in both oxidising and reducing atmospheres and may be considered as unsuitable for expansion in a rotary kiln, owing to the difficulty of controlling the temperature with sufficient accuracy to ensure bloating yet prevent adhesion.

Samples A3341/61, A3456/61, A1079/62 and A1082/62 have a bloating range of 50°C in an oxidising atmosphere and a bloating index of less than 60, and so are unlikely to be suitable for the manufacture of lightweight aggregate.

The clay samples A3455/61 and A3456/61 have a high bloating index but yield a bloated product of a rather friable nature with a moisture absorption of more than 20 per cent, which would probably not be acceptable.

The remaining clay sample, A3458/61, and 3 shale samples, A3342/61, A3344/61 and A3346/61, are recommended for pilot tests in a rotary kiln. The clay sample yielded 42.7 per cent of minus 10-mesh material when put through the jaw crusher (Table 4), so that the crushed material would have to be pelletised before firing. For this reason it would be easier to test the shale samples, and of these A3344/61 should be tested first since it has the highest bloating index. The bloating index of this sample is superior to that of the Victorian Silurian Shale, though the water absorption is slightly greater. There seems no reason why this sample should not make a satisfactory lightweight aggregate.

9. REFERENCES

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