Spodumene for Low Thermal Expansion

by M. J. Murray

^^lay bodies suitable for use in thermal shock situations require low or zero coefficients of thermal expansion. When spodumene (Li_20 Al_20_3 $5Si0_2$) is included in the body, it has the effect of altering thermal expansion behavior.

Spodumene occurs naturally as a monoclinic pyroxene known as alpha spodumene. When heated to above 1082°C (1980°F), it undergoes an irreversible volume increase of approximately 30% to form the tetragonal phase known as beta spodumene.

Within the past decade, a large deposit of spodumene ore in Western Australia was opened for commercial exploitation. It is claimed that this deposit is the largest source of high-grade spodumene in the world. The company, Gwalia Consolidated, Ltd., provided samples for the following tests:

Table 1
Typical Analyses of Body Components (% by weight)

	Alpha Spodumene Concentrate	NZ Halloysite	BBR Clay	Somerville Terra Cotta	Ball Clay C
SiO_2	64.50	50.70	60.90	60.50	72.00
$A1_2O_3$	26.00	35.80	25.40	18.60	16.40
Fe_2O_3	0.07	0.22	0.30	7.10	1.30
TiO_2	0.01	0.08	0.60	0.80	1.60
Li_2O	7.60	–	–	–	–
Na_2O	0.31	0.06	0.20	0.20	0.40
K_2O	0.12	0.05	0.40	2.30	1.80
CaO	0.05	0.07	0.20	–	0.50
MgO	–	0.06	0.30	0.70	1.00
LOI	1.34	12.96	12.10	8.90	4.80

Table 2
Plastic Body Compositions (% by weight)

	B1	B2	B3	B4	B5	B6	B7	B8	B9
Alpha Spodumene	50	50	50	50	40	40	40	40	50
BBR Clay	50	–	–	–	60	–	–	–	50
NZ Halloysite	–	50	–	–	–	60	–	–	–
Somerville Clay	–	–	50	–	–	–	60	–	–
Ball Clay C	–	–	–	50	–	–	–	60	–
Bentonite	3	3	3	3	3	3	3	3	–
Bentone 38	–	–	–	–	–	–	–	–	1.5

Plastic Body Trials

Analyses of spodumene ores from this deposit are detailed in Table 1, but because of time constraints only alpha spodumene concentrate was selected for this study.

Four clays of very different character were selected for blending trials. Adialyses of these clays are also given in Table 1. Two blending ratios were used for each clay, namely 40% spodumene and 50% spodumene by weight, producing eight test bodies.

Two additional bodies were included in these trials: Body 9, a minor variation on Body 1; and Body 10, a synthetic bone china body without spodumene (42% synthetic bone ash, 37% potash feldspar, 21 % kaolin and 2% Ben tone 38). Table 2 lists the compositions of the other test bodies.

The individual compositions were batched, then ball-milled with water for three hours. The milled body was then de-watered by pouring it into plaster molds. Upon reaching a plastic state, it was removed and stored in a sealed container to age for one week.

Next, half of each body was rolled into a slab of 10mm (less than ½ inch) thickness and cut into test bars of 30x130mm (approximately *V A X 5* inches), which were immediately marked at 100mm centers and allowed to air dry. When fully dry, they were measured to determine shrinkage.

The remaining half of the body was evaluated for its throwing properties using a potters wheel. Two standard bowl shapes, 120mm in diameter and 80mm in height, were made from each body. When leather hard, one bowl from each body was burnished to seal the surface and evaluate any benefits.

All the test bowls and bars (with the exceptions of B3 and B7) were fired together in a natural gas-fired kiln of 1-cubic-meter capacity to a temperature of 1300°C (2372°F). Firing atmosphere was maintained at neutral throughout the firing using an oxygen probe. Total firing time was 6 hours. Bodies B3 and B7 were fired to 1140°C (2084°F) in an electric kiln.

When the bars were cool, tests to measure the clays physical properties (including drying and firing shrinkage, flexural strength, water absorption, apparent porosity, bulk density and thermal expansion characteristics) were conducted. Five bars were tested for all bodies and results averaged.

Slip-Casting Body Trials

A terra-cotta body was selected as the basis for evaluating the influence of spodumene on casting slips. A line blending procedure was used to provide bodies with 1% increments in spodumene up to a total of 10%.

Table 3

Slip-Casting Body Compositions (% by weight)

	T1	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Somerville Clay	50	50	50	50	50	50	50	50	50	50	50
Kaolin	20	20	20	20	20	20	20	20	20	20	20
Potash Feldspar	10	10	10	10	10	10	10	10	10	10	10
Flint	20	20	20	20	20	20	20	20	20	20	20
Spodumene	–	1	2	3	4	5	6	7	8	9	10

Table 4

Subjective Evaluation of the Plastic Bodies

Body/Fired Color	Throwing Behavior	Turning Behavior	Burnishing Behavior
B1/cream	fair	good	poor
B2/white	fair	good	fair
B3/red	poor	poor	poor
B4/buff	fair	fair	poor
B5/cream	fair	good	poor
B6/white	fair	fair	poor
B7/red	poor	poor	poor
B8/fawn	fair	fair	poor
B9/cream	good	good	fair
B10/white	poor	poor	good

Eleven casting bodies were prepared and allowed to age for three days. The slip-casting body compositions are listed in Table 3. Slips were individually poured into plaster molds. Casting time was 10 minutes, after which all molds were emptied and incline-drained for an additional 10 minutes. The castings were removed from the molds after 24 hours, air dried, then collectively fired to 1140°C in an electric kiln.

Measurements were then taken for drying and firing shrinkage, water absorption and thermal expansion characteristics.

Plastic Body Results

A summary of all physical test results is presented in Table 5. Drying shrinkages were not excessive and all fell within the range 3%—7%; however, firing shrinkages were unusual. Indeed, there were firing expansions in seven cases—the result of the irreversible expansion of alpha to beta spodumene. The bone-china body BIO shows a typically high-firing shrinkage and contrasts the unusual behavior of alpha spodumene.

Flexural strength (modulus of rupture) was acceptable for stoneware applications. Most of the compositions showed strengths in this region. Bodies B5 and B8 were the strongest of the spodumene compositions.

All the bodies had high water-absorption figures, demonstrating the effect of the volume expansion of alpha spodumene at 1082°C. The lowest absorption was obtained from body B8.

Apparent porosity results were also high, the lowest porosity being obtained from body B8.

Bulk density results were low, as would be expected from bodies with high porosity values. The highest result was obtained from body B8.

The bodies achieved low and in most cases linear rates of expansion. The low-

Table 5

Summary of Physical Test Results

	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10
Firing Temperature (°C)	1300	1300	1140	1300	1300	1300	1400	1300	1300	1300
Drying Shrinkage (% Dry Length)	6.95	4.39	3.31	3.2	5.26	4.39	3.95	3.12	5.49	6.05
Firing Shrinkage (% Dry Length)	-5.42	-2.92	-8.59	-5.49	-0.22	0.43	-3.30	1.08	-3.69	14.62
Modulus of Rupture (MPa)	21.80	16.52	12.62	29.67	41.40	27.03	16.44	33.54	28.76	55.59
Water Absorption (% Dry Weight)	21.08	24.90	26.87	18.19	14.86	19.44	16.78	9.08	21.50	0.42
Apparent Porosity (% Total Volume)	35.02	40.80	44.72	30.81	24.78	32.05	28.10	15.80	35.52	0.69
Bulk Density	1.67	1.64	1.66	1.69	1.67	1.65	1.68	1.74	1.65	1.65
Thermal Expansion ($\times 10^{-6}$ @ 800°C)	2.25	2.50	3.00	1.88	2.66	2.81	3.75	2.50	2.25	9.38

est thermal expansion was achieved by body B4 with a coefficient of expansion of 1.88 X 10E-6 cm/cm between 20°C and 800°C (68°F and 1472°F).

Subjective evaluations of the throwing and burnishing behavior of the plastic bodies are presented in Table 4. The best bodies for throwing were Bl, B5 and B9, all containing ball clay, BBR and spodumene. Addition of the commercial plasticizer Bentone 38 improved the properties required for throwing.

Slip-Casting Body Results

Drying shrinkage values for all slip-casting bodies was 8% of dry length. The spodumene content had no noticeable effect.

Firing shrinkage for all slip-cast bodies was 15% of dry length. Again, the spodumene had no noticeable effect.

Water absorption steadily decreased from 4.93% to 0.66% with increasing spodumene content. The fluxing action of the lithium in the spodumene is clearly beneficial.

The thermal expansion of the base terra-cotta casting slip was progressively decreased with increasing spodumene content. The quartz anomaly at 573°C (1063°F) was notably reduced.

Applications

As a modifier of existing bodies, spodumene can provide better thermal expansion characteristics and reduced porosity. In this study, the addition of only small quantities of spodumene to a terra-cotta body reduced the porosity. Also, the sensitivity to rapid firing and cooling cycles was improved, thus permitting a faster rate of cooling and consequently a quicker kiln turnaround.

Furthermore, the addition of only small quantities of spodumene could assist in the precise lowering of the thermal expansion of a body to achieve a better fit between the body and some glazes. It would be of particular benefit where glaze shivering was a problem.

The unusual firing expansion encountered with alpha spodumene bodies could be useful in the production of products requiring zero or minimal dimensional change in firing; for example, prototypes for mold making.

Another suitable application would be for raku firing. Raku trials using spodumene-based bodies have demonstrated that they are superior to the conventional heavily grogged fireclay bodies. The loss rate was less, the bodies were structurally sound and, in many instances, could be used functionally. Another benefit was the improved glaze colors, which was attributed to the presence of lithium compounds in the body.

This color enhancement was also achieved from the same spodumene bodies without any glaze when they were in a wood-firing kiln together with a range of conventional bodies.

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