MINERAL TREATMENT OF SPODUMENE IN THE CERAMIC INDUSTRY. CHARACTERISATION ANDTECHNOLOGICAL USE

Roberto P. Hevia[(1)], Carlos Gil[(2)], Juan B. Carda[(2)]

[(1)]Instituto de Tecnología Minera (INTEMIN)–Servicio Geológico Minero Argentino (SEGEMAR), Buenos Aires (Argentina), roberto@inti.gov.ar
[(2)]Department of Inorganic and Organic chemistry, ESTCE, Universitat Jaume I de Castellón (Spain)

1. INTRODUCTION

In recent years, the branches of ceramics that have undergone the greatest development in the world have been those of floor and wall tile manufacture. This expansion has fostered the creation of companies dedicated to the manufacture of frits, glazes and ceramic pigments, together with marked growth in other already existing companies. On the other hand, the economic context in which the industrial activities are being conducted have led manufacturers to seek more efficient production technologies, among other processes including fast firing, single firing, etc. The focus has been on reducing costs, mainly for fuels and this requires refractory bodies with low dilatometric coefficients of expansion. For the manufacture of these refractories, as well for that of the frits mentioned previously, spodumene offers numerous advantages if it is included in their composition.

The thermal shock resistance of a ceramic body depends fundamentally on the following properties: thermal conductivity, coefficient of expansion, mechanical strength and modulus of elasticity. Of these properties, the one that can vary most is thermal expansion. This is the cause of the great interest in $Li_2O{\cdot}Al_2O_3{\cdot}SiO_2$ systems, which include compounds with very low coefficients of expansion, which allow making very thermally resistant pieces.

Spodumene is a lithium aluminosilicate $LiAl(SiO_3)_2$, which is found in the natural state as α–spodumene, structurally a monoclinic 'pyroxene' that contains 7.9% Li_2O and has a density of 3.2 g/cm^3. At high temperatures, 900º-1000ºC, this low temperature form undergoes an irreversible polymorphic transformation, increasing its volume and converting to β–spodumene, which belongs to the tetragonal crystalline system. In this form the mineral displays a density of 2.4 g/cm^3, and is characterised by exhibiting a very low dilatometric expansion, corresponding to values below $1.0{\cdot}10^{-6}$ ºC^{-1}.

On the other hand, spodumene has a very pronounced fluxing action, both of its own and because of the eutectics it forms with other fluxes. This property is used in the manufacture of frits for ceramic glazes and for earthenware. It is also very important for reducing the vitrification temperature and the final porosity of ceramic bodies. Beyond the applications of spodumene in the ceramic industry, the high percentage of lithium present in the mineral opens up numerous prospects for industrialisation; thus, lithium is considered worldwide as a strategic material for its great variety of applications: glass manufacture, lubricants, alloy obtainment, drug elaboration, operation of cooling systems, and in the manufacture of batteries.

The spodumene deposits correspond in all the cases, to pegmatites with a zoned structure, in which the mineral is located in the intermediate bands and the core. In the Argentine Republic, the main deposits are in the provinces of San Luis and Catamarca, and they are characterised by a great mineralogical variability. In all of these, spodumene is associated with: quartz, potassium feldspar, plagioclases-oligoclases and albite, muscovite and biotite, in addition to amblygonite and sometimes beryl. In relation to other pegmatites, a little participation of muscovite is observed and, in contrast, a greater one of albite.

For all these reasons, the objective of this work focuses on optimising the business operation of spodumene by development of an appropriate infrastructure and, in addition, to promoting knowledge in the mining field with respect to the numerous applications that beneficiated spodumene can have.

2. METHODOLOGY

The purpose of this work is to transmit the experience developed in an Argentine industry, in the mineral treatment of a spodumene-bearing pegmatite, for use in the manufacture of ceramic materials. The beneficiation of the mineral was done through a heat treatment and subsequent refining, producing the irreversible the α–β polymorphic transformation of spodumene, which is why its contribution to the microstructure of a ceramic body will increase its thermal shock resistance. Comparative physical, chemical and mineralogical studies were conducted with samples of natural lithium pegmatite from the El Alto area in the

Province of Catamarca and treated spodumene. Finally the effect of the spodumene addition to an earthenware body has been compared.

3. EXPERIMENTAL

The mineralogical analysis of natural pegmatite has been performed in a Bruker 4D diffractometer and enabled recognising the presence of several mineral substances (table 1).

SAMPLE	MAJOR COMPONENT	Minor COMPONENT
Pegmatite	Spodumene ($LiAlSi_2O_6$)	Quartz (SiO_2) Feldspar ($R_2O.Al_2O_3.6SiO_2$)

Table 1. Mineralogical analysis of the natural lithium pegmatite.

The chemical analysis of the gross spodumene (table 2) was carried out by wavelength-dispersive X-ray fluorescence for the major elements, using as sample preparation method the automatic fusion with lithium tetraborate as a flux and using Certified Reference materials for its calibration and validation, while the lithium determination was performed by acid digestion and subsequent determination by atomic absorption spectrometry.

Analyte	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	Li_2O
%	72.61	20.55	0.952	0.01	0.075	0.037	0.945	0.282	5.210

Table 2. Chemical analysis of the natural lithium pegmatite.

Taking as a reference the standard chemical analysis of a spodumene with a maximum lithium content, and that of a sodium feldspar (albite), an approximate mineralogical composition has been calculated (table 3). The results show that it has ≅ 40% impurities, which can be eliminated by appropriate treatment. In these impurities quartz predominates over the feldspar (7.6 % and 26.4% respectively).

Mineral components	%
Spodumene	62
Quartz	28
Feldspar	10

Table 3. Rational analysis of the natural lithium pegmatite.

When the spodumene is used in the composition of ceramic glazes and frits, in which this mineral contributes the chemical properties of its components, dry milling is the only treatment required to reach particle sizes below 70 µm. In contrast, when this mineral is used in ceramic bodies, it must previously be subjected to heat treatment (1100 °C), to avoid rupture of the ceramic body during the firing process.

During the calcination process the α–β spodumene inversion takes place, going from a hard and compact body to a quite crumbly body; the quartz in the pegmatite composition undergoes no transformation at all and some feldspar crystals begin to develop an incipient state of surface fusion that makes them harder and more resistant to any disintegration process. These observations have been the base for the elaborate of a project that enables the development of a β–spodumene , which stands out for its lithium content (%Li_2O > 6) and a dilatometric coefficient smaller than $1.0 \cdot 10^{-6}$ ºC^{-1}. The work consists of three basic steps; calcination at 1100 ºC, with an heating rate of 5ºC/min. and one hour soak at peak temperature, dry milling in a ball mill for 15 minutes, only to crush the spodumene, and subsequent selective sieving in a facility with a multiple mesh vibrator: ASTM No. 10, 30, 70 and 100. (Table 4).

ASTM mesh no.	Reject (%)	Through (%)
10	14	86
30	31	69
70	51.7	48.3
100	66.3	33.7

Table 4. Selective sieving of the treated pegmatite.

The most notable feature of this process is that the oversize on sieve mesh 10 consists mainly of quartz and feldspar. Though readily visible, this is then corroborated by the results presented in table 5, which correspond to the chemical analysis of the through material in each one of the four meshes used and their corresponding diffractograms (Figures 3, 4 and 5). The one corresponding to the natural sample without treatment is also added (figure 1) for comparison, to visualise the effects of the treatment in the spodumene beneficiation, showing that the quartz and feldspar peaks are minimised in the measurement as the mesh opening of the sieves used becomes smaller.

ANALYTE	Through # 10 (%)	Through # 30 (%)	Through #70 (%)	Through #100 (%)
SiO_2	63.35	61.95	61.48	61.45
Al_2O_3	28.22	29.07	29.11	29.14
Fe_2O_3	0.81	0.92	0.91	0.90
CaO	0.26	0.19	0.17	0.15
MgO	0.32	0.31	0.15	0.29
Na_2O	0.53	0.38	0.34	0.35
K_2O	0.23	0.13	0.12	0.11
Li_2O	6.14	7.04	7.46	7.55

Table 5. Chemical analysis of the through mesh fractions.

Comparing the results of tables 4 and 5, it is possible to relate the percentage of the through material corresponding to each mesh with the lithium law, as depicted in the following figure.

Spodumene is a mineral that lowers the thermal expansion of a ceramic body because it contributes its extremely low dilatometric coefficient and because its structure absorbs any free silica. This phenomenon occurs because spodumene forms a series of solid solutions between the composition $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$ and $Li_2O \cdot Al_2O_3 \cdot 8SiO_2$. In order to evaluate the effects that the addition of spodumene has on the thermal stability and therefore, on the coefficient of expansion of a ceramic body, a feldspathic earthenware body of "A" was prepared with a standard formulation, and in parallel another body "B" was prepared, which differed from the former in that it had a 10% treated spodumene addition in the composition.

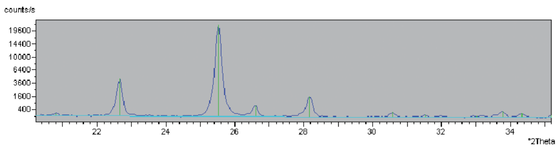

Figure 1. XRD "P#10"

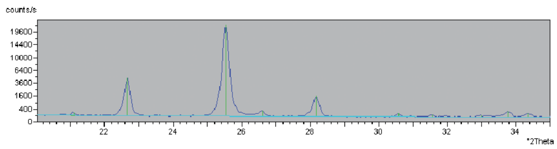

Figure 2. RD "P#30"

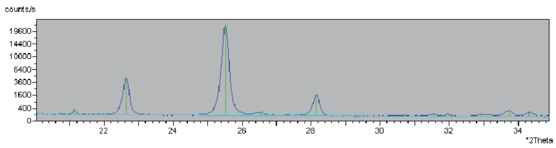

Figure 3. XRD "P#70"

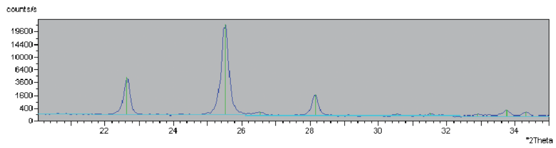

Figure 4. XRD "P#100"

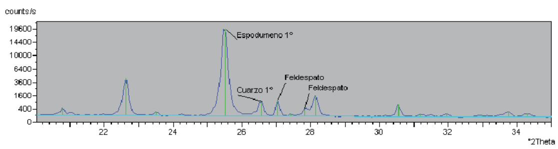

Figure 5. XRD "gross pegmatite"

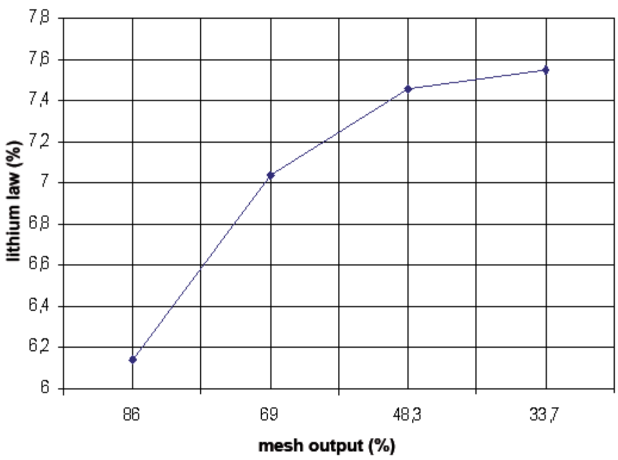

Figure 6. Relation: lithium law vs. sieve output.

Test specimens were made with both bodies, firing these at 1180ºC. Dilatometric studies were conducted in a Netzsch apparatus, in static air atmosphere with a heating rate of 5ºC/min. The results detailed below in table 6 show that a 10% addition of spodumene to an earthenware body can reduce its coefficient of expansion by 50%.

	Sample A (without spodumene)	Sample B (with spodumene)
Coef. expansion (20–800ºC)	$7.5 \cdot 10^{-6}$ ºC^{-1}	$3.2 \cdot 10^{-6}$ ºC^{-1}

Table 6. Coefficient of expansion of earthenware bodies.

5. CONCLUSIONS

- The thermal transformation of α-β spodumene with a change of density from 3.2 g/cm^3 to 2.4 g/cm^3, facilitates its separation from quartz and feldspar by selective sieving, since β-spodumene is concentrated in the finer sieving fractions.
- The coefficient of expansion of an earthenware body decreases strongly by adding β-spodumene to its composition.

6. ACKNOWLEDGEMENTS

The author wishes to thank Mr. Alfredo Inocencio, Mrs. Gloria Brunetti, Mrs. Ana Rodriguez Velo and Mr. Diego Pucciarelli, for their help in this work; thanks also go to the Project for the 'Improvement of the Efficiency and Competitiveness of the Argentine Economy', a Community (E.U.) cooperation project with the Argentine Republic.

REFERENCES

[1] Botto, I., Baran, E., Cohen Arazi, S., Krenkel, T. Aspectos estructurales de la espodumena en relación con el método de tratamiento ácido. Bol. Soc. Esp. Cer. y Vid., V15, Nº3, May/June 1976.

[2] Fishwick, J. Spodumene aids fast firing, improves bodies. Ceramic Industry Magazine p34, May 1967.

[3] González Peña, J.M. Materiales cerámicos de bajo coeficiente de dilatación a base de silicoaluminato de litio. Bol. Soc. Esp. Cer. y Vid., V7, Nº3, 1968.

[4] Hummel, F.A review of thermal expansion data of ceramic materials. Especially ultra-low expansion compositions. Interceram Nº6, p 27-30, 1984.

[5] Mc Cracken, D. Lithium minerals review 1993. Industrial minerals, p85-89, set/1994.

[6] Luis Sanchez-Muñoz, J.B. Carda Castelló. Enciclopedia cerámica: TOMOS 2.1 y 2.2. "Materias primas y aditivos cerámicos". 2002.

[7] Ginés F, Orenga A., Sheth A., Thiery D., "Ejemplo del espodumeno para fabricar pastas de gres porcelánico técnico" QUALICER 2004, Pág. 233-236.