Improving Technological Performances of Ball Clays: A Case-study from Patagonia (Argentina)

Abstract

Innovation in the ceramic tile industry is stressing properties like powder flowability and ability to toughen green tiles, so turning technological requirements of ball clays ever stricter in terms of plasticity, dispersion in water, rheological properties, workability in the green state, refractoriness and firing colour. Technological performance of ball clays have been improved by taking as benchmark the highest quality raw materials on the market. The mineralogy, plasticity, methylene blue index and ceramic behavior of the Patagonian ball clays are analogous to those of European clays, but improvement is needed to approach the highest quality materials. On this basis, four Patagonian deposits were selected and their characteristics enhanced by adding highly plastic corrective clays targeted on the benchmark. Porcelain stoneware formulations, containing improved ball clay mixes, were experimented at both laboratory and industrial scale. The improved ball clays behave like the best raw materials currently used, although modest changes occur in the mechanical properties, water absorption and whiteness of the fired products.

Keywords: *ball clay, porcelain stoneware tiles, Patagonian raw materials*

Introduction

The properties of ceramic raw materials need of continuous upgrading in order to meet the demand stemming from product innovation and quality improvement, particularly in the ceramic tile manufacturing, which is the success key of this industry [1–2]. Many new developments appear to be closely related to the quality of raw materials used [3–4].

The aim of this study is the improvement of technological performance of ball clays, taking Patagonian raw materials as a case-study, pursuing a new paradigm in the blend design. Instead of the best blend achievable with the raw materials available in the same deposit or mining district, the novel products have been designed, adding highly plastic clay materials, in order to match the technological behavior of the best ball clays on the market, which are taken as benchmark [5–7].

Such ball clays, especially suited for porcelain stoneware tiles, consist of kaolinite, interstratified I/S with a predominant illitic component and quartz. They are characterized by outstanding technological properties: high plasticity combined with proper slip rheological behavior, bestowing a high modulus of rupture on green and dry tiles as well as white or near white firing color [8–10]. The ceramic properties of Patagonian sedimentary clays are similar to those of the European ball clays, e.g. from Germany or France, having generally low to intermediate values of plasticity depending on the amount of non-plastic minerals and the occurrence of smectite together with kaolinite and interstratified I/S [11–12]. The Argentinian residual kaolins have low plasticity, but excellent whiteness [13–16].

Materials and Methods

Six raw materials coming from deposits in Patagonia were taken into account: four ball clays (Puma, Super, Frente A and Lote 8, Santa Cruz province) and two highly plastic clays: one sedimentary (FPS, Santa Cruz province) and one white bentonite (WB, Río Negro province). The four ball clays were selected trying to get the widest range of plasticity (in decreasing order: Puma, Super, Frente A and Lote 8). Their characteristics will be improved to achieve a technological behavior similar to that of benchmark clays. Further, the two corrective clays (FPS, WB) were chosen to improve the ceramic performance, particularly plasticity and firing color.

Blends were designed adding one highly plastic clay to one moderate plasticity clay in order to match the benchmark. The criteria followed are based on methylene blue index and/or plasticity values. Both clays and blends were characterized from the chemico-physical and technological viewpoints:

- chemical composition by XRF–WDS (Philips PW1480)
- mineralogical composition of the bulk sample (XRD-CuK, Rigaku Miniflex)
- particle size distribution by photo-sedimentation (ASTM C-958, Micromeritics SediGraph 5100)
- specific surface area by BET method (ASTM C-1069, Micromeritics FlowSorb II 2300)
- plasticity (Atterberg consistency limits, UNI10014)
- surface activity evaluated by methylene blue index (ASTM C-837)
- firing color by CIE-Lab colourimetry (Hunterlab MSXP-4000)
- microstructure by scanning electron microscopy (SEM JEOL 35 CF).

Once determined the clay properties and the ceramic behavior of blends, some porcelain stoneware batches containing improved ball clays were experimented at the laboratory scale simulating the industrial tilemaking process (50 mass-% of typical Na-K feldspar utilized in tilemaking was added to each clay and blend).

The tilemaking process was simulated by ball milling and slip drying, humidification and pelletizing,

Chiara Zanelli, Mariarosa Raimondo, Guia Guarini, Michele Dondi
CNR-ISTEC, Istituto di Scienza e Tecnologia dei Materiali Ceramici, Faenza, 48018, Italy

Claudio Iglesias
Piedra Grande SA, Trelew, Chubut, 9100, Argentina

Eduardo Domínguez
Departamento de Geologia, Universidad Nacional del Sur, Bahia Blanca, 8000, Argentina

Rosa Ullmann
LOSA SA, Olavarría, 7400, Argentina

Corresponding author:
Michele Dondi
E-mail: michele.dondi@istec.cnr.it

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Tab. 1
Chemical and mineralogical composition of raw materials and benchmark clays

Constituent [mass-%]	Patagonian Ball Clays				Plastic Additives		
	Frente A	Super	Lote 8	Puma	WB	FPS	Benchmark Clays
SiO_2	65,53	64,55	69,80	62,97	66,12	58,22	56–60
TiO_2	0,50	0,48	0,12	0,66	0,15	0,61	1–1,5
Al_2O_3	22,41	22,94	20,00	22,19	12,80	21,50	22–25
Fe_2O_3	0,87	0,83	0,27	1,26	1,05	3,34	1–2
MgO	0,23	0,23	0,02	0,26	3,66	0,54	~0,5
CaO	0,19	0,25	0,06	0,31	0,90	0,56	0,3–0,5
Na_2O	0,01	0,01	0,01	0,09	1,19	0,35	0,3–0,5
K_2O	0,88	0,63	0,54	0,56	0,33	1,24	2–3
S	<0,01	<0,01	0,01	0,01	0,04	<0,01	~0,02
C	0,11	0,06	0,05	0,27	0,04	0,14	~0,1
L.o.I. [%]	9,58	9,87	8,38	10,89	13,45	13,50	7,94
Kaolinite	56	57	59	60	–	52	58–72
Int. I/S	traces	4	–	5	–	–	6–10
Smectite	–	–	–	–	76	20	–
Quartz	43	39	41	35	4	28	22–32
Cristobalite	–	–	–	–	19	–	–

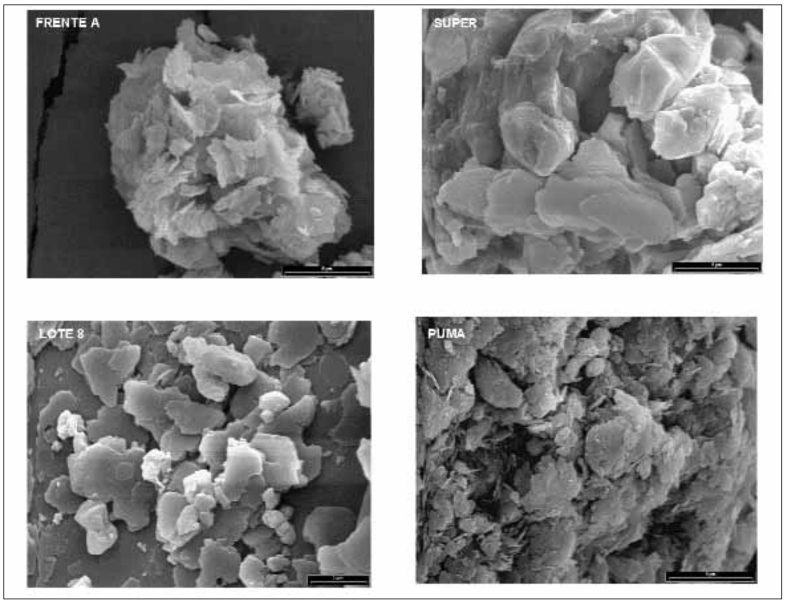

Fig. 1
SEM micrographs of Patagonia ball clays

uniaxial pressing (40 MPa) of 110 mm × 55 mm × 5 mm tiles, drying in an electric oven and firing in an electric roller kiln (maximum temperature 1200 °C, 51 min cold to cold). Technological properties and ceramic behavior were assessed on both semifinished and fired products: bulk density of green body, firing shrinkage (ASTM C-326), water absorption (ISO 10545-3), dry and fired bending strength (ISO 10545-4) and firing color (ISO 10545-16). Best formulations were tested on an industrial pilot line.

Results and Discussion

Clay Characterization

The mineralogical composition of the low to moderate plasticity ball clays from Patagonia consists basically of kaolinite (around 55–60 %), quartz (around 35–43 %) and a low amount (1–5 %) of expandable clay minerals, i.e. randomly interstratified illite/smectite (Tab. 1).

The microstructure of these ball clays presents kaolinite crystals with irregular border, ranging from 5 to below 1 µm in size (Fig. 1). The two plastic clays are characterized by smectite predominat over cristobalite in the bentonite while associated to kaolinite and quartz in the case of FPS.

The benchmark (high quality ball clays) has a larger amount of kaolinite (60–70 %) and interstratified I/S (5–10 %) but a lower percentage of quartz (20–30 %) with respect to Patagonian clays.

The chemical composition of the Patagonian ball clays is comprised in the following ranges: SiO_2 63–70 %; Al_2O_3 20–23 %; Fe_2O_3 <1,3 %; K_2O and TiO_2 ≤1 %; MgO, CaO and Na_2O ≤0,3 %. The main differences concern silica and potash amounts, which are higher and lower, respectively, than the benchmark composition. The corrective clays are characterized by a larger amount of iron oxide (FPS) or MgO and Na_2O (WB). The Patagonian clays have low (Lote 8) to moderate plasticity values (Frente A, Super, Puma) which are considerably lower than the benchmark for the MBI and Atterberg plastic index (Tab. 2).

The corrective clays have very high plasticity, especially the bentonite, with MBI and PI up to twice the benchmark values. The Patagonian ball clays have a wide range of particle size distribution: the poorly plastic Lote 8 is coarse-grained, while the moderately plastic ball clays are similar to the benchmark. The very plastic clays have a <2 µm fraction as high as 85 % in the case of FPS, while the bentonite is not particularly fine-grained (Fig. 2).

The values of specific surface area follow substantially those of particle size distribution: being lower than the benchmark (24–34 m²/g) in the case of Lote 8, Frente A and Super, but higher for Puma, FPS and particularly WB (Tab. 2).

Once fired at 1200 °C, the Patagonian ball clays exhibit a brightness value L* from 82 (Puma) to 95 (Lote 8) in good inverse relationship with the iron content. These values are much higher than the benchmark. The highly plastic clays are distinctly darker with a consistent decrease of L* (Tab. 3).

Characteristics of Blends

The blends were designed adding one highly plastic clay to one of the moderately plastic ball clays, supposing the plasticity behavior is an additive property, so that mixing two different clays results in proportional values of the main technological properties.

This assumption is confirmed, as shown in Fig. 3, by the good correlation of predicted values of colloidal fraction, plasticity, methylene blue index and specific surface exhibit with the experimental ones. This approach enabled to design and achieve technological properties quite similar to the benchmark values (Fig. 3).


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		Methylene Blue index [meq/100 g]	Specific Surface Area [m²/g]	Plastic Limit (WP) [mass-%]	Liquid Limit (WL) [mass-%]	Plastic Index (IP) [mass-%]
Patagonian Ball Clays	Frente A	10	22	26	38	12
	Super	11	23	25	38	13
	Lote 8	2	3	23	30	7
	Puma	19	30	26	50	24
Plastic Additives	WRNB	65	81	43	155	112
	FPS	36	45	30	115	85
Benchmark Clays		15–20	25–35	30–35	60–80	30–50

Tab. 2 Technological properties of raw materials and benchmark

Properties		L*	a*	b*	Fe_2O_3
Patagonian Ball Clays	Frente A	89,1	1,2	10,2	0,9
	Super	90,0	1,8	10,3	0,8
	Lote 8	94,6	0,6	4,0	0,3
	Puma	82,5	0,1	14,8	1,3
Plastic Additives	WB	62,6	2,2	18,5	1,1
	FPS	70,9	0,7	13,0	3,3
Benchmark Clays		71–83	0,5–2,0	10–15	0,8–1,5

Tab. 3 Firing color determined by CIE-Lab of raw materials and benchmark

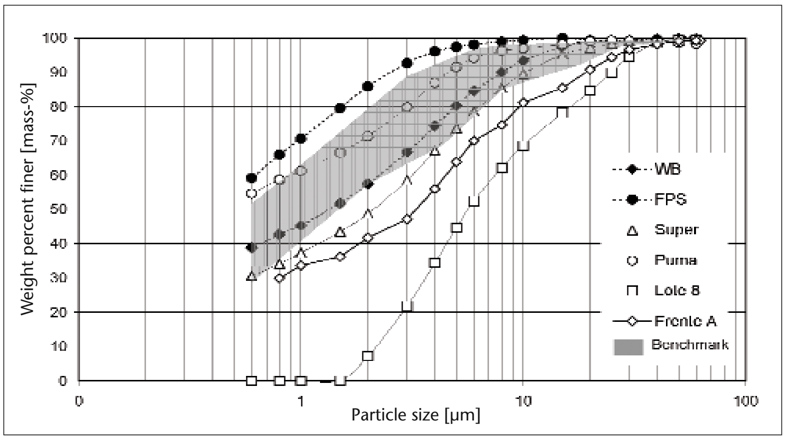

Fig. 2 Grain size distribution of Patagonia ball clays

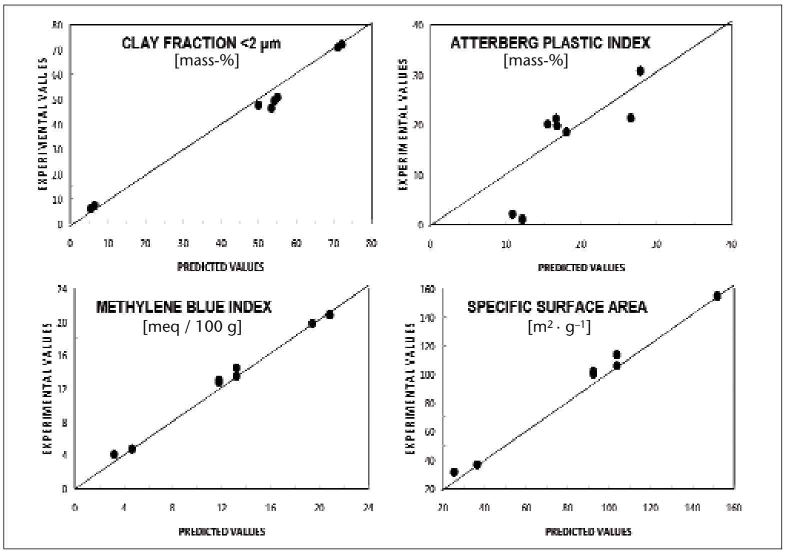

Fig. 3 Correlation between the predicted and experimental values of technological properties of clay mixtures designed by different blending criteria

Porcelain Stoneware Batches

The main technological properties evaluated in the porcelain stoneware bodies are summarized in Tab. 4.

All the porcelain stoneware tiles exhibit a larger firing shrinkage with respect to the benchmark. It is likely due to a different compaction of agglomerate powders. The water absorption varies in a wide range (0–1 mass-%) depending on the raw clay, as not every formulation can be sintered as easily as the benchmark. The addition of highly plastic clays affects the firing behavior by promoting the sintering: a drastic lowering of water absorption occurs together with an increase of shrinkage and bulk density. In general, the white bentonite has a stronger effect, even if in one case the clay FPS resulted more effective.

The batch based on the easily sinterable Puma clay is slightly affected by the addition of FPS, but it turns overfired with 5 % bentonite, as suggested by the slight decrease of firing shrinkage. Batches made up of moderately plastic clays unexpectedly exhibit a different behavior. Frente A is fluxed by WB and particularly by FPS, resulting in a water absorption value from 1,2 % down to ≤0,2 %.

In contrast, little changes occur when the batch based on Super is additivated with WB or FPS. The batch prepared with the poorly plastic clay Lote 8 is refractory and, although the addition of FPS and especially WB is able to significantly promote its densification, the water absorption persists >4 %.

The color of porcelain stoneware bodie turned darker by using smectite-rich plastic additives, likely due to increasing content of chromophores and glassy phase.

Industrial Scale Trials

Three porcelain stoneware bodies were experimented at a pilot line: a reference batch and two formulations with improved blends of Patagonian clays. The technological properties of semifinished and fired porcelain stoneware tiles are reported in Tab. 5.

Bodies A and B exhibit a different compaction during pressing, causing a larger porosity of unfired tiles, which implies a lower drying modulus of rupture, as a higher water absorption and firing shrinkage with respect to the reference.

Nevertheless, the fired modulus of rupture is similar to the reference, despite the higher porosity, indicating a strengthening of the ceramic body. The firing color presents higher L* values for bodies A and B, but the different water absorption turns difficult any direct comparison.

Tab. 4 Technological properties of the porcelain stoneware bodies

		Bulk Density [g/cm³]	Water Absorption [mass-%]	Firing Shrinkage [cm/m]	Firing Color		
					L*	a*	b*
Porcelain Stoneware Bodies	F	2,3	1,17	7,0	77,1	5,4	5,9
	S	2,3	1,32	6,3	78,3	6,4	7,1
	L8	2,0	11,17	6,5	86,4	6,6	–0,5
	P	2,3	0,10	6,5	72,9	4,3	8,4
	W	2,0	0,05	4,5	59,5	7,0	16,8
	F1	2,0	0,03	6,5	75,9	4,0	6,7
	F5W	2,3	0,21	7,0	76,4	5,4	5,8
	F5F1	2,3	0,01	6,0	75,3	5,3	6,8
	S5W	2,3	0,94	6,0	76,8	6,4	7,0
	S5F1	2,3	1,23	7,0	76,8	6,3	7,5
	L85W	2,2	4,85	7,5	85,5	6,4	-0,2
	L85F1	2,0	7,69	7,3	83,2	6,4	0,1
	P5W	2,3	0,02	6,3	72,7	4,3	8,3
	P5F1	2,3	0,04	6,5	71,8	4,2	8,7
	Benchmark	2,3–2,4	<0,1	5–6	–	–	–

Formulation [mass-%]	Reference	Body A	Body B
Typical industrial ball clay	50	–	–
Frente A	–	47,5	47,5
FPS	–	2,5	–
WB	–	–	2,5
Feldspar	50	50	50
Properties			
Drying modulus of rupture [MPa]	5,0	4,2	4,5
Firing shrinkage [%]	4,42	4,92	5,1
Water absorption [%]	0,3	4,9	4,1
Firing modulus of rupture [MPa]	34,4	32,6	29,8
Color L* [CIE-Lab]	79,1	86,1	86,1
Color a* [CIE-Lab]	1,4	1,2	1,2
Color b* [CIE-Lab]	13,4	11,4	10,9

Tab. 5 Industrial trial of porcelain stoneware bodies with improved ball clay blends

Conclusions

Technological properties of ball clays can be improved, through accurate design and blending, by exploiting highly plastic clays as additives in order to get products particularly suited for large size porcelain stoneware tiles.
Special attention must be paid to the criteria for a correct blending, since not every clay property scales linearly with the additive amount (mostly depending on its mineralogical composition). As plasticity is a key-factor in ball clays for porcelain stoneware, batch design was essentially based on methylene blue index and plasticity values, but further variables must be considered (e.g. content of chromophores affecting sintering behaviour and final colour of the ceramic product).

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