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Raw clays processing for ceramic pastes

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ABSTRACT

Ceramic products are mainly produced with clays supplied by mineral industry, that have in general very heterogeneous compositions. In order to cope with industrial requirements, producers must apply a controlled blending policy of the different geological formations, which can lead to the rejection of a large percentage of reserves. An alternative solution is the use of processing plants. However, clays are hard to process materials, mainly due to their ultra fine grain sizes. So, the development of a suitable processing flow sheet is always a challenging task.

This paper presents the results of an experimental research study of beneficiation of two raw clays from a large deposit in Spain. The objective of the study was to improve the physical and technological properties of the ceramic pastes by reducing the colouring elements (mainly iron and titanium minerals) in the raw clays. This target was achieved by screening, hydrocycloning and froth flotation. A column flotation was used with very good results in the beneficiation of one of the raw clay types. The research study was divided in two parts: laboratory scale tests leading to the establishment of a suitable flotation chemical environment, followed by pilot scale tests. A final flow sheet was developed and the data for scaling up to an industrial plant was acquired. The complex column flotation process was controlled by means of a sophisticated controller based on fuzzy logic inference.

Keywords: Clay; Ceramic; Froth flotation; Fuzzy logic inference

1. INTRODUCTION

Ceramics are inorganic non-metallic solids that are subjected to high temperature in manufacture and/or use. The most common ceramics are composed of oxides, carbides and nitrates, although silicates, borides, phosphates, tellurides and selenides can be used, as well. Traditionally, ceramic products are produced from unrefined clays and combinations of refined clays and powered or granulated non plastic minerals.

The quality of the raw clays in deposits is far from being constant. Their chemical/mineralogical compositions present, usually, very large deviations, due to the heterogeneous nature of the different geological formations exploited. One of the major problems is the high content of iron and titanium oxides (colouring elements) and organic matter of some clays, that forces to reduce drastically the allowed weight percentage of these clays in the final mixed clays. To meet the physical/technological specifications of ceramic industry, raw clays producers must use an efficient blending policy of the different deposits. However, one consequence of this blending policy is an important reduction of the mining reserves.

In order to meet the constantly changing demand and the stringent specifications of the ceramic industry, raw clays producers were constrained to consider processing of raw clays as an unavoidable step in their producing flow sheets. Therefore, due to their hard-to-process characteristics, there are not well established procedures for the physical/chemical separation of this ultra fine material.

Among the available mineral processing technologies, flotation is undoubtedly the most suitable to separate minerals of very fine grain size, allowing a wide range of working conditions that can be adapted to the variability of the clays characteristics.

The aim of this study was the reduction of the iron/titanium grade (siderite, magnetite and goethite) of two raw clays, from an important deposit in Spain with large geologic reserves, from 3.5-6% to a grade bellow 2% in iron+titanium. The study consisted in bench flotation tests for the definition of the flotation formulae, followed by pilot plant tests in order to determine a final flow sheet and to acquire data for the scaling up to an industrial plant.

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In the bench scale tests a mechanical cell was used, while the pilot tests were carried out in a flotation column. This last process is well adapted to process very fine materials, due to the higher residence time of these particles inside flotation columns compared with conventional mechanical cells of the same volume (Yianatos *et al.*, 1987; Finch and Dobby, 1990). Before flotation, a pre-treatment stage consisting of screening and hydroclassification is mandatory.

2. EXPERIMENTAL

2.1. Raw clays characterisation

The raw clays, that for the sake of confidentiality are designated by type V and type Z, are composed mainly by illite and kaolinite, containing, as well, quartz, feldspars and some colouring elements such as siderite, magnetite and goethite. Table 1 gives the chemical compositions of the samples used in the bench and in the pilot tests.

Table 1
Typical chemical analysis of V and Z clay types

		SiO_2 %	Al_2O_3 %	K_2O %	Na_2O %	Fe_2O_3 %	TiO_2 %
Bench tests	V type clay	58.46	21.28	2.41	0.15	3.97	0.95
	Z type clay	65.45	18.63	1.26	0.17	5.31	1.35
Pilot tests	V type clay	57.46	23.76	2.64	0.15	3.53	1.01
	Z type clay	66.8	15.31	1.04	0.09	5.79	1.36

V type raw clay is a homogeneous grey clay with some dark particles of a large size range, mostly constituted by organic material. There are two distinct classes that can be separated by the 40μm sieve. The coarser fraction (+40μm) is a brown sand, containing 45% of the total Fe_2O_3 in carbonate and oxide form, with some quartz grains and mica plates and also kaolinitic clay. The finer fraction (-40μm) contains mainly clay minerals with some iron in the form of chlorite.

Z type raw clay is a reddish heterogeneous clay characterised by a bimodal particle size distribution, with some coarser particles among a mass of very fine clay particles (Table 2). The coarser fraction (+80μm) is a brown sand containing siderite, hematite and goethite. The micaceous minerals are concentrated in the two intermediate classes (-80+40μm). Iron predominates in the coarser fraction (10% of the overall mass with 20% of the total Fe_2O_3) while the fraction -40μm (90% in weight of the raw clay) is mainly composed of clay minerals, kaolinite, illite and quartz, containing low iron content, mainly as chlorite.

Table 2
Particle size distribution of V and Z clay types

	+ 80μm %	- 80μm+63μm %	-63μm+40μm %	-40μm %
V type clay	7.2	1.2	1.8	89.9
Z type clay	7.2	1.8	3.0	87.9

The particle size analysis shows that 80% of the cumulative mass is finer than 5μm in V type clay and 10μm in the Z type clay.

2.2. Bench flotation tests

Bench flotation tests were carried out using a Leeds laboratory flotation cell provided with impeller speed and air flow rate controls. One of the particularities of this cell is that the impeller is driven from the bottom of the cell, leaving the top surface, where the froths are formed, free from turbulence. However, due to the low density of the raw clay particles, some undesired turbulence was inevitably generated on the surface. To avoid this, the height of the original cell was increased by fitting an extra body to the cell. The resulting capacity was 2.75L.

Before the flotation step, a pre-treatment stage consisting of screening and hydroclassification is mandatory. Several preliminary tests were conducted for the set-up of the flotation formulae. The best results were achieved with three flotation stages intercalated with conditioning. Figs. 1 and 2 depict the flow sheets corresponding to the best results in the processing, respectively, of V type and Z type clays (Durão *et al.*, 2000).

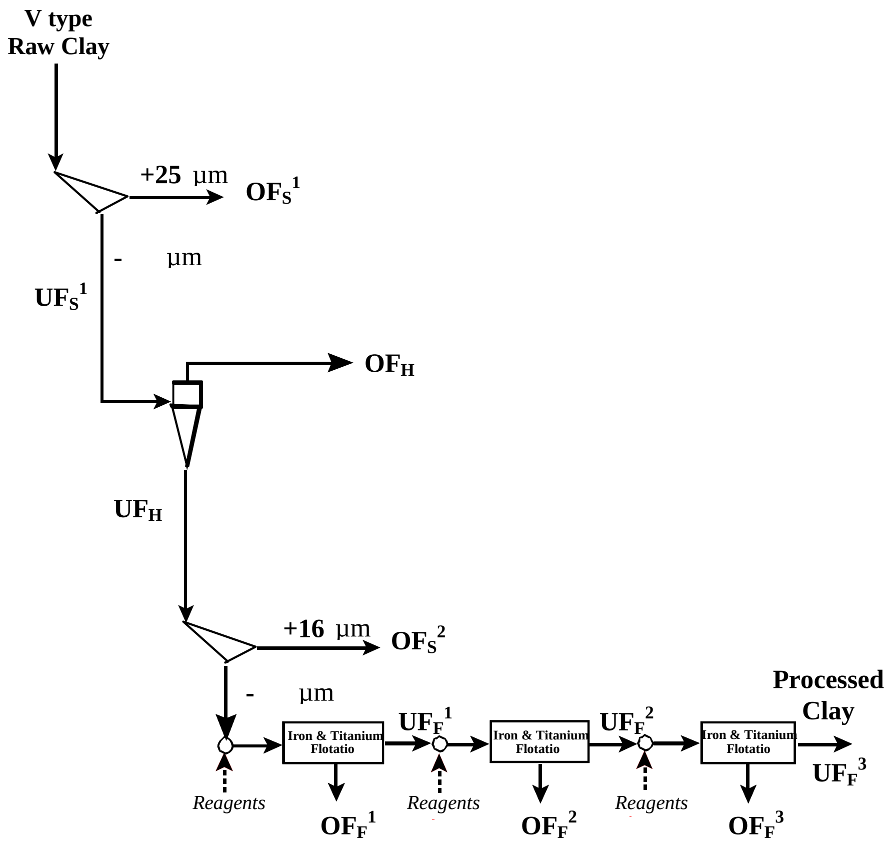

Figure 1. Bench scale tests flow sheet – V type clay

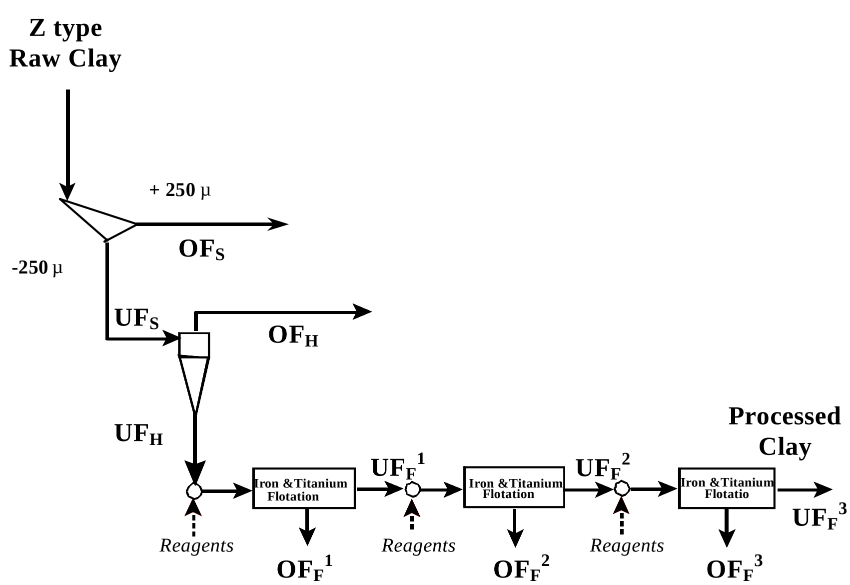

Figure 2. Bench scale tests flow sheet – Z type clay

The chemical reagents used were sulphonate collectors for the iron minerals (Aerofloat® 825 and Aerofloat® 845N, from Cytec) and fuel oil. The acidic environment was provided by sulphuric acid. The operational conditions of the two clay types differed only in the conditioning time: 5min for the V type and 10min for the Z type (Table 3).

Table 3
Operating conditions and flotation reagent dosages - bench tests

Unit Operation	Conditions	Time min
Conditioning #1	50% solids by weight H_2SO_4 @ pH=3.0 Aero 825= 250g/ton Aero 845= 250g/ton Fuel oil = 500g/t	5/10*
Iron/Titanium Flotation	15% solids by weight H_2SO_4 @ pH=3.0	10
Conditioning #2	H_2SO_4 @ pH=3.0 Aero 825= 125g/ton Aero 845= 125g/ton Fuel oil = 250g/t	10
Iron/Titanium Flotation	15% solids by weight H_2SO_4 @ pH=3.0	10
Conditioning #3	H_2SO_4 @ pH=3.0 Aero 825= 125g/ton Aero 845= 125g/ton Fuel oil = 250g/t	10
Iron/Titanium Flotation	15% solids by weight H_2SO_4 @ pH=3.0	10

* V type clay – 5min; Z type clay – 10min

2.3. Pilot plant tests

The results of the bench flotation tests lead to the establishment of two different pilot plant flow sheets to process the two types of raw clays. While for Z type clay, froth flotation is indispensable to reduce the iron grade, V type clay was not significantly enriched by flotation. V type clay was therefore processed only by screening and hydroclassification.

2.3.1. V type clay

The flow sheet used to process the V type clay is depicted in Fig. 3. Both hydrocyclones were fed with 20% of solids in weight. Different working conditions of the equipment were tested and evaluated. The best results were achieved with the settings shown in Table 4.

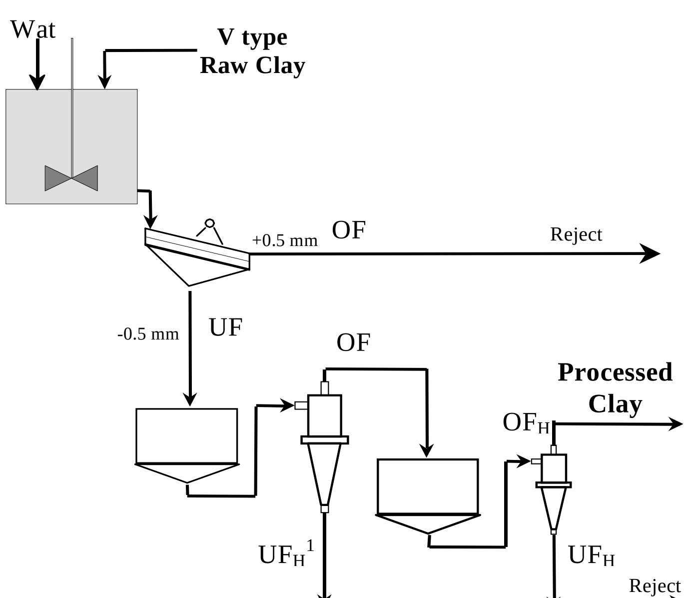

Figure 3. Pilot scale tests flow sheet – V type clay

Table 4
Working conditions of the pilot plant equipment – V type processing

Equipment	Settings	Equipment	Diameter
Wet screen	Opening – 0.5mm Length – 1220mm Width – 360mm Inclination – 10°	Hydrocyclone I	Cyclone – 51.2mm Vortex – 11.1mm Apex – 3.2mm
		Hydrocyclone II	Cyclone – 25.4mm Vortex – 5.5mm Apex – 1.5mm

2.3.2. Z type clay

After several preliminary tests, a suitable processing flow sheet was established to process the Z type clay. The final flow sheet is shown in Fig. 4. The raw clay is processed by screening, classification, in a spiral classifier, hydrocycloning and column flotation.

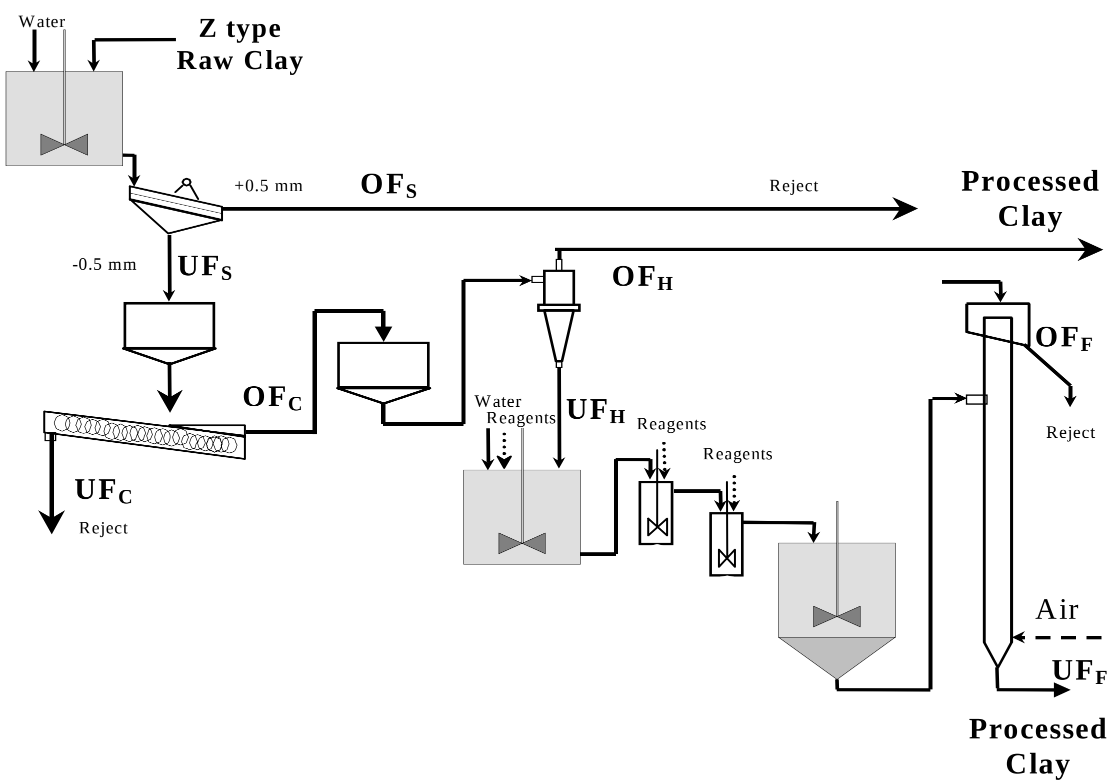

Figure 4. Pilot scale tests flow sheet – Z type clay

The flotation column is a tube in acrylic of 80mm diameter by 3.2m height. The feed is introduced at about 1/3 of column height from the top and air is introduced some centimeters above the bottom end by a porous sparger.

Column flotation is a complex multi-variable process that needs automatic control to run in stable conditions. It was not possible to develop an accurate and simple dynamic mathematical model usable in the synthesis of a classical controller (Carvalho *et al.*, 1999), therefore a supervisory controller based on fuzzy logic inference (Fig. 5) was designed. The fuzzy controller uses a heuristic rule data base (Carvalho and Durão, 2002).

The objective of the top level control is to keep the iron and titanium content of the underflow stream close to the target value. This level of control acts on the set points of three intermediate process variables: air holdup in the collection zone, collection zone height and bias water flow rate. These variables are controlled by the manipulation of the air, washing water and underflow rates.

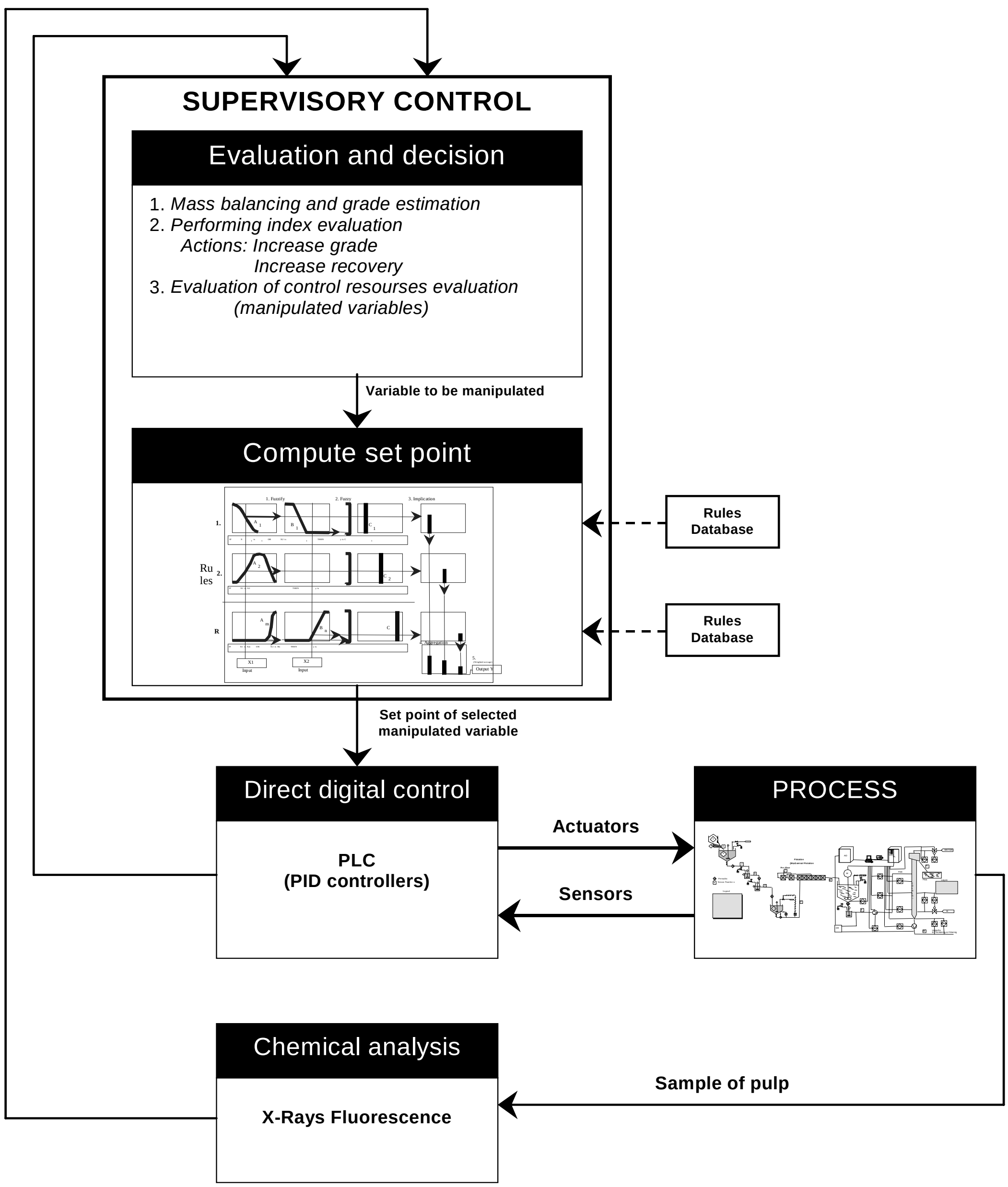

Figure 5. Schematic diagram of the supervisory control system of the flotation column

Air holdup in the collection zone and the collection zone height are calculated from measurements on two pressure sensors mounted on the column wall. The value of the bias water flow rate is approximated by the difference between underflow and feed flow rates (corrected for the variation of the froth depth).
The feed flow rate and the manipulated variables flow rates are measured with different flow meter types and their control is achieved by direct manipulation of the speed of peristaltic pumps and by the opening of the valves, using local PID controllers at the lowest level of control. The grades of feed and underflow streams are analysed by an on stream analyser.

Several tests were performed to tune the equipment. The best results were achieved with the operational conditions shown in Table 5. The hydrocyclones and the flotation column were fed with 20% solids in weight, while the conditioning stage before flotation was done with 50% solids in weight. The reagents and respective concentrations were the same used in the bench flotation tests. The pH was kept equal to 2.5 by addition of sulphuric acid during conditioning and flotation. The conditioning time was 10 minutes.

Table 5
Working conditions of the pilot plant equipment – Z type processing

Equipment	*Settings*	*Equipment*	*Settings*
Wet screen	Opening – 0.5mm Length – 1220mm Width – 360mm Inclination – 10°	Hydrocyclone (diameter)	Cyclone – 51.2mm Vortex – 14.5mm Apex – 3.2mm
Spiral classifier	Length – 950mm Inclination – 20° 50-70rpm *Decantation zone* Height – 120mm Width – 95mm	Flotation column (nominal values)	Q_A – 270L/h Q_U – 70L/h ε_c – 16.5% Froth zone height-370mm

3. RESULTS AND DISCUSSION

3.1. Bench scale tests

Table 6 shows the best results obtained with V type clay in the bench scale tests. The very fine cut by hydrocycloning permits the recovery of a product (OF_H), representing about 80% in weight of the raw clay, with a low Fe_2O_3 grade (2.82%). The product *Processed Clay* is the mixture of the flotation underflow (UF_F) with the overflow of the hydrocyclone (OF_H). The processed clay, representing about 90% of the raw clay, presents a grade of 2.79% Fe_2O_3. However, the titanium grade could not be reduced.

Table 6
Best results of bench tests – V type clay

	Wt (%)	Assays (%)						Distribution (%)					
		SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	TiO_2
Feed	100.0	58.46	21.28	2.41	0.15	3.97	0.95	100.00	100.00	100.00	100.00	100.00	100.00
OF_S^1	4.6	30.70	5.00	0.11	0.10	26.74	0.19	2.39	1.07	0.21	3.03	30.65	0.91
UF_S^1	95.5	59.78	22.06	2.52	0.15	2.89	0.99	97.61	98.95	99.81	95.45	69.48	99.47
OF_H	81.8	56.90	25.40	2.77	0.17	2.82	1.02	79.64	97.66	94.04	92.73	58.12	87.85
UF_H	13.6	77.08	1.98	1.04	0.02	3.30	0.80	17.96	1.27	5.88	1.82	11.32	11.47
OF_S^2	0.4	51.80	9.10	1.27	0.03	21.23	0.51	0.36	0.18	0.22	0.08	2.19	0.22
UF_S^2	13.2	77.86	1.76	1.03	0.02	2.75	0.81	17.61	1.09	5.65	1.76	9.16	11.27
OF_F^1	1.4	70.30	8.60	1.41	0.03	3.71	0.97	1.66	0.56	0.81	0.28	1.29	1.41
OF_F^2	0.4	71.10	10.60	1.54	0.11	3.64	1.15	0.54	0.22	0.28	0.32	0.40	0.53
OF_F^3	0.4	67.50	9.80	1.44	0.07	3.04	1.19	0.40	0.16	0.21	0.16	0.27	0.44
UF_F	11.1	79.40	0.30	0.95	0.01	2.58	0.76	15.01	0.16	4.36	0.74	7.18	8.84
Processed Clay (OF_H+ UF_F)	92.9	59.58	22.41	2.55	0.15	2.79	0.99	94.64	97.82	98.40	93.47	65.30	96.69

Despite the numerous tests carried out with different flotation conditions, iron and titanium minerals of this raw clay could not be significantly reduced by froth flotation. It should be pointed out that 80% of the cumulative mass of V type clay is finer than 5μm. As can be seen in Fig. 6, the kinetics of iron minerals is very slow and the weight percentage rejected in the floated product is very low (Fig. 7).

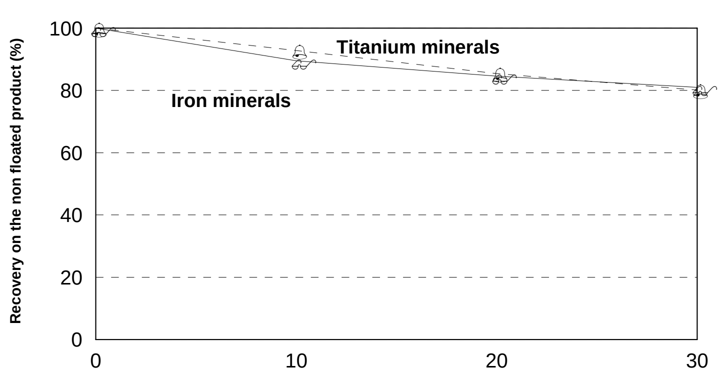

Figure 6. Kinetic curve – V type clay

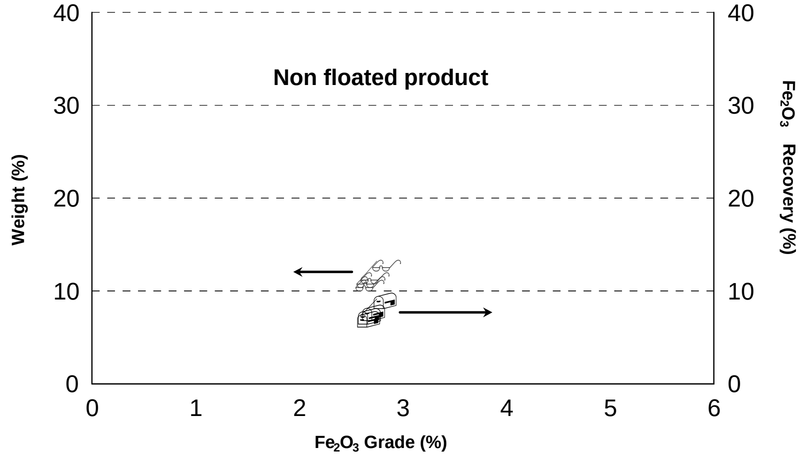

Figure 7. Washability and grade- recovery curves – flotation of V type clay

In what concerns Z type clay, the results obtained (Table 7) showed that it is possible to reduce significantly the iron grade by using froth flotation.

Table 7
Best results of bench tests – Z type clay

	Wt (%)	Assays (%)						Distribution (%)					
		SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	TiO_2
Feed	100.0	65.45	18.63	1.26	0.17	5.31	1.35	100.0	100.0	100.0	100.0	100.0	100.0
OF_H^1	62.3	54.85	26.24	1.66	0.23	5.22	1.37	52.20	87.73	81.77	82.77	61.20	63.09
UF_H^1	37.7	82.98	6.06	0.61	0.08	5.47	1.32	47.80	12.27	18.23	17.23	38.80	36.91
OF_H^2	53.1	51.70	28.44	1.74	0.24	5.25	1.34	41.94	81.06	73.11	75.18	52.50	52.67
UF_H^2	9.2	73.00	13.51	1.19	0.14	5.02	1.53	10.26	6.67	8.66	7.60	8.70	10.42
OF_F^1	3.9	69.50	7.77	0.53	0.18	10.82	5.99	4.14	1.63	1.64	4.14	7.95	17.29
OF_F^2	2.8	73.30	7.47	0.48	0.10	11.06	3.26	3.14	1.12	1.06	1.65	5.83	6.76
OF_F^3	2.6	78.50	6.60	0.45	0.09	9.05	1.77	3.12	0.92	0.93	1.38	4.43	3.41
UF_F	28.4	86.20	5.64	0.65	0.06	3.85	0.45	37.40	8.60	14.61	10.05	20.59	9.46
Processed Clay (OF_H^2+ UF_F)	81.5	63.72	20.49	1.36	0.18	4.76	1.03	79.34	89.66	87.71	85.23	73.09	62.13

As it can be seen in Fig. 8, the iron and titanium minerals have much faster responses to flotation than V type clay. It was possible to recover by flotation almost 30% of the clay with an Fe_2O_3 grade around 3.85% (Fig. 9).

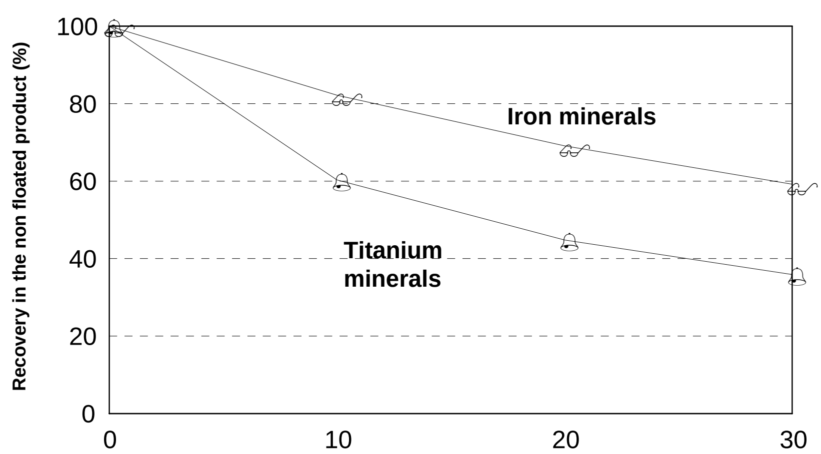

Figure 8. Kinetic curve – Z type clay

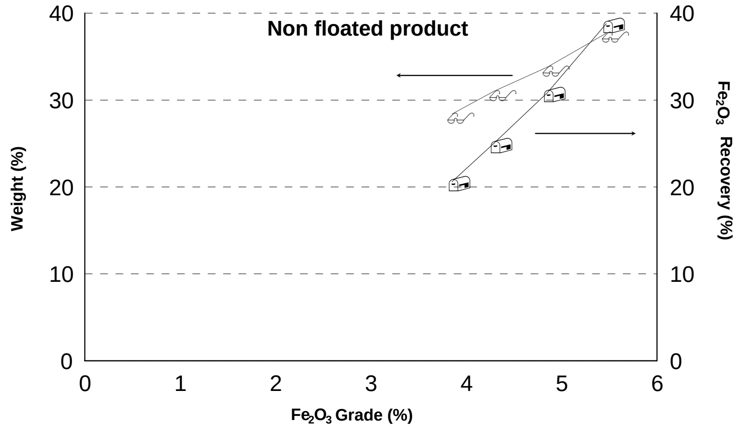

Figure 9. Washability and grade-recovery curves – flotation of Z type clay

The very fine fraction of the raw clay, amounting almost 50%, is very rich in iron and the overflow of the 2nd hydrocyclone increases significantly the grade in iron of the product Processed Clay (OF_H^2+UF_F).

Although not satisfying yet the targets (to reduce the iron/titanium grade to a value under 2%), the results of the bench flotation tests were encouraging, as it was possible to reduce about 1% in the iron grade, which represents a considerable amount of material.

3.2. Pilot plant tests

The best results, achieved with the flow sheets depicted in Figs. 3 and 4, and by using the operational conditions shown in Tables 4 and 5, are presented in Tables 8 and 9, respectively, for V and Z type clays.

Table 8
Best results of Pilot plant tests - V type clay

	Wt (%)	Assays (%)						Distribution (%)					
		SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	TiO_2
Feed	100.0	57.46	23.76	2.64	0.18	3.53	1.01	100.00	100.00	100.00	100.00	100.00	100.00
OF_S	3.7	57.20	22.30	2.39	0.17	6.72	0.93	3.68	3.47	3.35	3.50	7.04	3.41
UF_S	96.3	57.47	23.82	2.65	0.18	3.41	1.01	96.32	96.53	96.65	96.49	92.96	96.59
OF_H^1	68.3	53.00	21.55	2.32	0.27	2.46	0.66	63.00	61.93	60.11	42.73	47.57	44.82
UF_H^1	28.0	68.37	29.36	3.44	0.14	5.72	1.87	33.32	34.59	36.54	53.76	45.38	51.77
UF_H^2	8.6	65.50	17.00	2.14	0.15	3.70	0.96	9.80	6.15	6.97	7.44	9.01	8.17
Processed Clay (OF_H^2)	59.7	51.20	22.20	2.35	0.14	2.28	0.62	53.20	55.78	53.14	46.32	38.56	36.65

Table 9
Best results of Pilot plant tests - Z type clay

	Wt (%)	Assays (%)						Distribution (%)					
		SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	K_2O	Na_2O	Fe_2O_3	TiO_2
Feed	10.0	66.80	15.32	1.04	0.09	5.79	1.36	100.00	100.00	100.00	100.00	100.00	100.00
OF_S	13.0	60.10	11.40	0.76	0.06	15.76	1.20	11.70	9.68	9.51	8.23	35.39	11.50
UF_S	87.0	67.80	15.90	1.08	0.10	4.30	1.38	88.30	90.32	90.49	91.77	64.61	88.50
OF_C	85.8	68.30	15.60	1.08	0.11	4.29	1.38	87.73	87.40	89.24	99.56	63.57	87.28
UF_C	1.2	52.70	7.50	0.39	0.00	21.87	0.91	0.95	0.59	0.45	0.00	4.53	0.80
OF_H	64.8	62.30	19.70	1.39	0.11	4.48	1.47	60.44	83.35	86.74	75.19	50.14	70.22
UF_H	21.0	77.86	1.76	1.03	0.02	2.75	0.81	24.48	2.41	20.83	4.43	9.97	12.54
OF_F	2.5	73.30	6.30	0.49	0.34	6.13	3.95	2.74	1.03	1.18	8.97	2.65	7.28
UF_F	18.5	84.95	1.00	0.30	0.02	3.69	0.90	23.53	1.21	5.34	3.90	11.79	12.27
Processed Clay (OF_H+ UF_F)	83.3	67.33	15.55	1.15	0.09	4.30	1.34	83.96	84.56	92.09	79.09	61.93	82.49

In what concerns V type clay the results, although not attaining the target values, could be considered as sufficient. The processed clay (OF_H^2), constituting 60% in weight of the raw clay, presents 2.28% grade in Fe_2O_3 and 0.26% in TiO_2. Almost 50% of the Fe_2O_3 could be rejected.

Z type clay, with much higher iron and titanium contents than V type clay, can be easily processed in terms of iron minerals but not in terms of titanium minerals. It could be recovered more than 80% of the feed in the processed clay (a mixture of the hydrocyclone overflow (OF_H) with the non floated material (UF_F)) with a Fe_2O_3 grade of 4.3%. It was possible to reject more than 20% of Fe_2O_3.

4. CONCLUSIONS

The objective of this study was to process two raw clays from important deposits in Spain with high iron/titanium contents and very fine grain size. The industrial objective was to obtain an iron/titanium grade bellow 2%. This objective was a challenging one.

Although the proposed target was not completely accomplished, a reduction of the content in colouring elements could be achieved. In what concerns Z type clay, a raw clay with almost 6% in Fe_2O_3 and 80% of its mass finer than 10μm, the best results were achieved through a combination of size separation by screening and hydrocycloning, followed by froth flotation of the iron/titanium bearing minerals of the underflow products by using sulfonate based collectors in an acidic circuit. The final product is a mixture of the non floated product with the hydrocycloning overflow product. A 1.5% decrease in Fe_2O_3 grade was achieved in a product that represents 83% in weight of the raw clay.

V type clay, with a grade in Fe_2O_3 of almost 4%, being 80% of its mass finer than 5μm, could not be upgraded by froth flotation. However, more than 40% by weight of the iron minerals could be removed with a simple fine size separation flow sheet, although the Fe_2O_3 content of the final product could not be decreased to less than 2.3%.

ACNOWLEDGEMENTS

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NOMENCLATURE

	Subscripts	Superscripts
OF – Overflow,	H – Hydrocyclone	1 – 1st step
Oversize, Floated	F – Flotation	2 – 2nd step
UF – Underflow,	S – Screen	3 – 3rd step
Undersize, Unfloated	C - Classification (spiral)	

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