CHARACTERISATION OF "LA SERRATA" CLAY USED IN THE FEBEX PROJECT

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1. INTRODUCTION

This report presents the results obtained in CIEMAT laboratories during the characterisation phase of the montmorillonite from Serrata de Níjar (Almería) for the FEBEX Project. The parameters and characteristics specified in the procedure 70-IMA-G-3-05 have been determined. Although clay coming from the same quarry has been used in CIEMAT over the last eight years (reference S-2), having been thoroughly characterised, a confirmation of the key properties is required to evaluate the validity of previous results (Rivas et al. 1991, Villar et al. 1995).

2. PROCESSING OF THE CLAY AND SAMPLING

The pile of clay extracted from the quarry underwent an homogenisation process that is described in RUÍZ & VILLAR (1996a). The main phases of this process were: extension of the piled clay for air drying, ploughing and grooving of the clay several times and manual extraction of rock fragments. At this point samples were taken and analysed to check the homogeneity. As it was satisfactory, the clay was taken to the factory of Minas de Gádor at Almería. A total of 610 Tm were processed there according to the procedures described in RUÍZ & VILLAR (1996b): the clay was first smashed in a helix grinder to disintegrate the remaining lumps, and then dried in a rotary oven to water contents around 14%. Afterwards, it was sieved by a 5 mm screen and directly packed into big-bags through a hopper. At the time the material was falling into the big-bags, samples of approximately 10 kg were taken every 2.4 Tm and a reference was assigned to all of them: 70-IMA-3-4-#, being # a correlative number from 1 to 119. These samples were introduced in plastic bags and taken to CIEMAT laboratories where half of each was mixed to the others to obtain approximately 620 kg of an homogeneous sample of reference 70-IMA-3-4-0. Parts of this sample were sent to the other participating institutions for its use in their laboratory tests:

- 17 kg to CSIC-Zaidín (Granada)

- 85 kg to Clay Technology (Lund, Sweden)

- 120 kg to UPC (Barcelona)

Ten of the unmixed samples have been chosen and tested to verify the variability of parameters through the whole lot.

Table I: Samples of processed material selected for analysis

Reference[1]		Date	Hour	Lot[2]	Big-bag[3]	Analysis
70-IMA-003-04-2	F-2	1-2-96	10:00	1	3	* ♣ #
70-IMA-003-04-4	F-4	2-2-96	10:30	2	7	
70-IMA-003-04-17	F-17	5-2-96	09:50	3	28	

Reference[1]		Date	Hour	Lot[2]	Big-bag[3]	Analysis
70-IMA-003-04-18	F-18	5-2-96	10:10	3	30	* #
70-IMA-003-04-22	F-22	5-2-96	12:30	3	38	
70-IMA-003-04-37	F-37	7-2-96	15:50	5	68	* ♣ #
70-IMA-003-04-58	F-58	8-2-96	16:30	7	110	*
70-IMA-003-04-59	F-59	8-2-96	16:47	7	112	
70-IMA-003-04-65	F-65	9-2-96	09:10	9	124	*
70-IMA-003-04-75	F-75	9-2-96	11:47	11	144	* ♣ #
70-IMA-003-04-79	F-79	9-2-96	15:55	11	152	
70-IMA-003-04-93	F-93	12-2-96	12:18	13	180	*
70-IMA-003-04-102	F-102	12-2-96	17:20	15	198	* #
70-IMA-003-04-109	F-109	13-2-96	11:25	17	212	*
70-IMA-003-04-119	F-119	13-2-96	17:27	20	232	* ♣ #

[1]Hereafter, only the last figure of the reference will be given
[2]Processing lot
[3]Big-bag which is being filled when the sample is taken
*: water content, Atterberg limits, specific surface, granulometry, specific weight, X-ray diffraction of the bulk sample and of oriented aggregates (O.A.)
♣: Chemical analysis of the bulk sample
#: swelling pressure, hydraulic conductivity, thermal conductivity, suction/water content relationship, soluble ions, free silica, exchangeable complex

Besides, five aliquots of the homogeneous sample 70-IMA-3-4-0 have been taken and analysed to confirm the results previously obtained. The reference of these samples is A-1 to A-5.

3. RESULTS OBTAINED

The samples analysed have not been submitted to further processing in the laboratory. The water content has been determined and the samples have been kept in closed plastic bags. The basic parameters have been determined, i.e. Atterberg limits, granulometry, specific surface and specific weight, as well as the mineralogical and chemical composition. Hydraulic and thermal properties have been also examined in samples compacted uniaxially to dry densities of 1.70 and 1.60 g/cm^3, which are the dry densities of the blocks after compaction and of the installed clay barrier once it has swelled and filled the voids of the repository, respectively.

3.1 Basic properties

Atterberg limits have been determined following the Procedure 70-IMA-G-0-12. A liquid limit of 103 ± 4 % has been obtained.

The specific surface has been measured using the BET method (Procedure 70-IMA-G-0-11), in which the adsorbing gas, nitrogen, does not occupy the interlamellar space, thus it is referred to external surface. A Flowsorb II 2300 apparatus of Micromeritics has been used. A value of 33 ± 3 m^2/g has been obtained.

The specific weight is determined using classical picnometers and bidistilled water as suspension medium following the procedure 70-IMA-G-0-09. A value of 2.70 has been obtained.

To determine the granulometric distribution the sample is hydrated with distilled water plus sodic hexametaphosphate during 18 hours. It is dispersed by alternating cycles of agitation and ultrasound and the granulometry of fine particles (under 74 µm) is determined by sedimentation according to the Stokes law (Procedure 70-IMA-G-0-06). The remaining particles are sieved through a battery of screens from 2 mm to 74 µm (Procedure 70-IMA-G-0-05). The resulting granulometric curves are shown in Fig. 1.
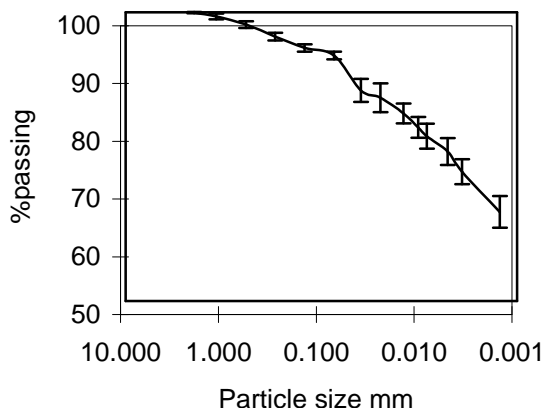
Fig. 1: Average granulometric curve of the 11 samples analysed, with indication of the standard deviations

Table II summarises the basic properties of the analysed samples, which can be considered similar to those previously determined for S-2 clay, except for the specific weight, which is lower than that determined for S-2 (2.78), and the liquid limit which is lower for the FEBEX clay.

Table II: Basic properties of the analysed samples

Sample	w %	<74µ %	<2µ %	wl %	wp %	Ip	Specific weight	Specific surface m^2/g
F-2	14.8	93	65	103	52	49	2.75	28

Sample	w %	<74µ %	<2µ %	wl %	wp %	lp	Specific weight	Specific surface m^2/g
F-4	15.1			105	53	48		31
F-17	16.0	92	69	100	53	46		34
F-18	15.0	92	67	111	53	48	2.62	38
F-22	15.1			110	52	51		35
F-37	13.3	93	69	100	52	51	2.67	35
F-58	11.9	92	59	101	54	47	2.75	30
F-59	12.7	92	66					31
F-65	11.9			108	51	47	2.77	26
F-75	11.7	92	63	96	51	45	2.68	32
F-79	12.3			101	50	51		33
F-93	13.1	93	64	104	47	57	2.73	26
F-102	14.1	93	66	103	52	51	2.65	33
F-109	11.9	93	66	100	47	53	2.72	34
F-119	12.3	93	67	103	51	52	2.70	35
AVERAGE	13.4	93	65	103	51	50	2.70	32
STD. DEV.	1.5	1	3	4	2	3	0.05	3
A-1	14.4			98	54	44		28
A-2	14.7			98	55	52	2.68	30
A-3	14.4			98	55	47	2.75	32
A-4	14.3			100	60	50	2.72	32
A-5	14.5			98	58	42		29
AVERAGE	14.5			98	56	47	2.72	30
STD. DEV.	0.2			1	3	4	0.04	2

3.2 Mineralogy and chemistry

The mineralogical characterisation has been carried out on 10 samples of different big-bags and on 5 aliquots of the homogenised sample 70-IMA-3-4-0 (A-1 to A-5). The chemical analysis has been performed on 4 samples of different big-bags and on the aliquots A-1 and A-5.

3.2.1 Mineralogical analysis

3.2.1.1 Methods

The material was prepared by drying 50 g of each sample at 60°C and grinding them in an agate mortar to a grain size <60 µm.

The mineralogical characterization of the essential minerals was determined in the bulk sample by X-ray diffraction (XRD), using a PW 1370 Philips diffractometer and the powder method on a flat-rotating sample holder. The exploration velocity has been 2°/min with 2θ in

the range between 2 and 70°. The semiquantification was carried out using the reflecting factors shown in Table III (Schultz 1964, Barahona 1974).

Table III : Reflections and reflecting factors

Mineral	Reflection (Å)	Reflecting factor
T. Phyllosilicates (smectite)	4.45	0.1
Quartz	3.34	1.5
K-feldspar	3.24	1
Plagioclase	3.18	1
Cristobalite	4.07	0.6
Tridimite	4.3	0.6
Calcite	3.03	1

The accessory minerals were determined by a scanning electron microscope (SEM) coupled to an energy dispersive X-ray analysis system (EDX), after being identified and separated by stereoscopic microscope.

The thermal characteristics of the bulk sample have been determined in two samples using a Perkin-Elmer 1700 DTA equipment, at a scan rate of 10°C/min under air dynamic atmosphere (40 cm^3/min) at temperatures between 40 and 980 °C.

The <2 μm fraction has been obtained by suspension and decantation. 50 g of each sample were introduced in a test tube with desionized water during 24 hours. After this time, the clay in suspension is introduced in a glass. To obtain the <2 μm fraction, a vacuum filter apparatus was used to extract the water and retain the clay. This process is repeated until the material in suspension is wasted (approximately 10 days). After this process, oriented clay mineral aggregates are prepared (OA) and treated with ethylene glycol (EG), sulfoxide dimethyl (SD) and heated at 300° and 550°C to determine the clay minerals in the < 2 μm fraction by XRD.

3.2.1.2 Bulk sample

The semiquantitative mineralogical composition of the bulk sample is shown in Table IV. These results show that the principal mineralogical association in all the samples is formed by smectite (Sm), quartz (Qz), plagioclase (Plag) and cristobalite (Cri). K-feldspar (K-Fd), tridimite (Tri) and calcite (Cc) usually appear as traces. Smectite is the main mineral and its content varies between 81 and 96%. The other minerals are very scarce, they represent from 5 to 20% of the bulk sample and are considered as inherited minerals from the original volcanic rock. The XRD diagrams of the different samples are shown in Annex I.

Table IV: Semiquantitative mineralogical composition of the bulk sample

Sample	Sm%	Qz%	Plag%	Cri%	KFd%	Tri%	Cc%
F-2	89	2	2	2	0	1	1
F-18	92	2	3	3	0	Tr	Tr
F-37	92	3	2	2	Tr	Tr	Tr
F-58	96	2	1	1	Tr	Tr	Tr

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Sample	Sm%	Qz%	Plag%	Cri%	KFd%	Tri%	Cc%
F-65	94	2	2	2	0	Tr	Tr
F-75	89	3	4	2	0	Tr	2
F-93	95	1	2	2	Tr	2	Tr
F-102	95	2	2	1	0	Tr	Tr
F-109	93	1	3	2	0	Tr	Tr
F-119	92	2	2	3	1	Tr	Tr
AVERAGE	93±2	2±1	3±1	2	Tr	Tr	Tr
A-1	81	3	10	Tr	3	Tr	2
A-2	94	1	1	2	0	1	Tr
A-3	95	1	1	3	0	Tr	1
A-4	92	3	2	2	1	Tr	Tr
A-5	96	2	2	3	0	Tr	Tr

The DTA curves show an important endothermic peak at 130°C followed by an accessory peak at 200°C, due to the loss of moisture. A second endothermic at 640°C corresponds to the loss of structural OH⁻ of montmorillonite and another endothermic peak at 860°C can be interpreted as structural changes in clay. These diagrams, which are shown in Annex I, correspond to a dioctahedral montmorillonite-type smectite (MacKenzie 1970).

Among the accessory minerals detected by SEM are: carbonates (dolomite, calcite, barite-celestine), phosphates (apatite, xenotime, monacite), oxides (ilmenite, magnetite), micas (sericite, biotite, chloritized biotite), silicates (zircon, plagioclase, Al-silicates with Fe and Mg, quartz and opal) and sulphurs (pyrite).

Comparing this mineralogical composition with that obtained by Pérez del Villar (1989) and Pérez del Villar et al. (1991), the main difference observed is that the only phyllosilicate detected in the FEBEX clay is smectite, while in these previous studies traces of mica were detected. The new ATD diagrams follow the same pattern than those of former studies, except for an exothermic peak at 355°C which was attributed to the existence of Fe gel by Pérez del Villar (1989) and does not exist now.

3.2.1.3 <2 µm fraction

The mineralogical composition of the <2µm fraction indicates that the samples are almost pure smectite: the peak observed in the untreated O.A. at 14.5 Å shifts to a very strong reflection at about 16.9 Å when treated with ethylene glycol and when heated at 300º it collapses to 10 Å.

The XRD diagrams of the treated and untreated O.A., obtained at CIEMAT and UAM for comparison purposes, are shown in Annex I.

3.2.2 Chemical analysis

3.2.2.1 Methods

The chemical characterisation was performed in 4 unmixed samples and in 2 samples of the mixed clay. The samples were prepared by drying 200 g of each sample at 60°C and grinding them in an agate mortar to a grain size <60 μm.

The analytical methodology was carried out by: inductively coupled plasma-atomic emission spectrometry (ICP-AES) for Al_2O_3, $Fe_2O_{3\ total}$, Na_2O, MgO, MnO, TiO_2, CaO, P_2O_5, Ba, Ce, Co, Cr, Cu, La, Ni, Sr, V, Y and Zn; X-ray fluorescence (XRF) for SiO_2, on beads, and Rb, Th and U, on powdery samples; flame atomic emission spectroscopy (FAES) was used for K_2O and Li; organic and mineral carbon, and S were determined using a Leco CS-244 elemental analyser; FeO by Sánchez-Ledesma's et al. (1990) method, and F^- and Cl^- by selective ion electrode. H_2O^- and weight loss (WL) by TGA, using a Perkin-Elmer TGS-2 equipment.

3.2.2.2 Major elements

The results of the chemical analyses of the major elements are shown in Table V.

Table V: Chemical composition of the bulk sample

Oxides	F-2 %	F-37 %	F-75 %	F-119 %	AVERAGE %	STD. DEV.	A-1 %	A-5 %
SiO_2	58.6	59.4	59.2	60.5	59.4	0.8	59.9	58.7
Al_2O_3	18.2	18.4	17.8	18.1	18.1	0.3	16.6	17.9
Fe_2O_3	2.93	2.96	2.96	2.87	2.93	0.04	2.66	2.90
FeO	0.24	0.22	0.22	0.21	0.21	0.02	0.22	0.18
MgO	4.2	4.3	4.1	4.2	4.2	0.1	3.9	4.2
MnO	0.04	0.04	0.04	0.04	0.04	0.00	0.04	0.04
CaO	1.8	1.9	2.0	1.8	1.9	0.1	1.7	1.8
Na_2O	1.3	1.4	1.4	1.4	1.4	0.1	1.2	1.3
K_2O	1.1	1.1	1.1	1.0	1.1	0.1	1.0	1.0
TiO_2	0.23	0.24	0.25	0.23	0.24	0.01	0.22	0.23
P_2O_5	0.02	0.03	0.02	0.03	0.02	0.00	0.02	0.02
H_2O^-	7.5	6.0	7.6	6.0	6.8	0.9	12.0	7.0
H_2O^+	4.4	4.6	4.8	4.9	4.7	0.2	4.0	4.8
CO_2org	0.40	0.37	0.40	0.33	0.37	0.03	0.29	0.33
CO_2min	0.26	0.22	0.26	0.22	0.24	0.02	0.37	0.26
SO_2T	0.22	0.10	0.16	0.16	0.16	0.05	0.36	0.12
F^-	0.18	0.18	0.18	0.19	0.18	0.01	0.18	0.18
$F\equiv O$	0.08	0.08	0.08	0.08	0.08	0.00	0.08	0.08
TOTAL	101.6	101.5	102.4	102.3	102.0	0.5	104.7	101.0

A high homogeneity has been observed between the chemical composition of the different samples studied. The contents of CO_2min are low, which confirm the low percentage of carbonates. Comparing these results with those obtained by Pérez del Villar (1989) and Pérez del Villar et al. (1991), the samples analysed in this report have lower contents in

Fe_2O_3, MgO, CaO and CO_2org. The lower content in Fe_2O_3 could explain the lower specific weight of the FEBEX clay with respect to that of the S-2 clay.

3.2.2.3 Trace elements

The results of the chemical analyses of the trace elements are represented in Table VI.

Table VI: Trace elements in the bulk sample

Element	F-2 ppm	F-37 ppm	F-75 ppm	F-119 ppm	AVERAGE ± STD. DEV.	A-1 ppm	A-5 ppm
B_{tot}							
$^{10}B/^{11}B$	0.2500	0.2506	0.2466		0.249±0.002	0.2453	0.2453
Ba	135	180	190	160	166±24	150	195
Be	<5	<5	<5	<5	<5	<5	<5
Br	2.2	2.3	2.2	2.5	2.3±0.1	2.5	2.1
Ce	64	68	65	71	67±3	64	62
Cl^-	590	605	600	592	597±7	580	575
Co	15.0	8.2	8.3	8	9.9±3.4	8.3	8.7
Cr	7.2	7.9	5.9	6.4	6.8±0.9	11.0	6.4
Cs	10.0	11.0	9.8	9.6	10.1±0.6	10.0	10.0
Cu	20	28	14	39	25±11	30	31
Eu	0.76	0.79	0.79	0.83	0.79±0.03	0.75	0.75
I	<2	<2	<2	<2	<2	<2	<2
La	42	43	40	43	42±2	38	41
Li	55	58	55	55	56±2	54	54
Mo	<5	<5	<5	<5	<5	<5	<5
Nd	25	28	27	29	27±2	26	27
Ni	19	21	16	22	20±3	24	21
Rb	40	41	44	39	41±2	44	41
Re	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sn	<10	<10	<10	<10	<10	<10	<10
Se	<1	<1	<1	<1	<1	<1	<1
Sr	215	225	245	250	224±17	190	220
Th	20.1	20.1	19.2	20.1	19.9±0.5	19.0	19.7
U	1.5	2.6	1.3	2.2	1.9±0.6	1.9	1.9
V	16	16	19	16	17±2	12	14
W	<25	<25	<25	<25	<25	<25	<25
Y	20	24	23	25	23±2	23	22
Zn	62	71	60	69	66±5	64	70

The trace elements detected in the samples studied in this paper are similar to that given by Pérez del Villar et al. (1991), except for Cu, whose content is 25 ppm in the FEBEX samples, while it was not detected by the above mentioned authors, and for Cr, whose content was higher (15 ppm).

3.2.3 Structural formula

The chemical analyses of the <2μm fraction have been carried out in the samples A-1 and A-5, after saturating with Ca to homoionise the cation exchange complex.

The results obtained (Table VII) show that the chemical composition of both samples is very similar. They have lower contents in MgO and Na_2O and higher content in CaO than those studied by Pérez del Villar et al. (1991).

Table VII: Chemical composition of the homoionised < 2µm fraction

OXIDES(%)	A-1	A-5	AVERAGE
SiO_2	60.51	60.17	60.34
Al_2O_3	19.14	19.41	19.27
Fe_2O_3	3.26	3.46	3.36
FeO	0.17	0.14	0.155
MgO	4.04	4.22	4.13
CaO	3.57	3.50	3.53
Na_2O	0.28	0.35	0.31
K_2O	0.61	0.67	0.64
Ti_2O	0.18	0.17	0.17
H_2O^+	8.25	7.90	8.07

The structural formula has been calculated taking into account that the anionic charge is -44, with ideal anion composition O_{20} $(OH,F,Cl)_4$. The structural formulae of smectites A1 and A-5 are represented in Table VIII.

Table VIII: Structural formulae of the smectites

SAMPLE	TETRAHEDRAL		OCTAHEDRAL					INTERLAYER		
	$Si4^+$	Al^{3+}	Al^{3+}	Fe^{3+}	Fe^{2+}	Ti^+	Mg^{2+}	Ca^{2+}	Na^+	K^+
A-1	7.85	0.14	2.78	0.32	0.02	0.02	0.78	0.49	0.07	0.10
A-5	7.80	0.20	2.76	0.34	0.01	0.02	0.82	0.49	0.09	0.11

Smectite A-1 has an octahedral charge of -1.02 and a tetrahedral charge of -0.18, being the tetrahedral charge percentage of 15. The interlayer charge is 1.15.

Smectite A-5 has an octahedral charge of -0.96 and a tetrahedral charge of -0.20, being the tetrahedral charge percentage of 17. The interlayer charge is 1.18.

Both smectites have an aluminic dioctahedral layer structure, with Mg in octahedral sites, and 15% of charge of sample A-1 and 17% of charge of sample A-5 caused by tetrahedral substitution. Consequently these smectites are Wyoming-type montmorillonites (according to Schultz, in A.C.D. Newman, 1987).

The cation exchange capacity of the < 2 μm fraction has been calculated for the samples A-1 and A-5 according to the following method:

$$C.E.C. (meq/100g) = (1000 \text{ x } \%Ca^{2+} \text{ x valence}) / P.m.$$

The results obtained are 127 meq/100g for A-1 and 125 meq/100g for A-5.

3.2.4 Soluble salts and free silica

The content of soluble salts has been determined in a 1:4 extract, following the Procedure 70-IMA-G-0-29. 2.5 g of dry sample were dispersed in 10 cm^3 of distilled water and stirred for 48 hours. Then the suspension was centrifuged and chlorides and sulphates were determined in the supernatant by ion chromatography, as well as the electric conductivity, which was measured with an electrometric cell. The salt content is always under 1%, as it does not appear in the X-ray determinations.

Free silica was extracted in a 0.1M Na_2CO_3 solution after 48 hours stirring (Procedure 70-IMA-G-0-33). Afterwards the suspension was centrifuged and silica was measured in the supernatant by the silico-molibdic colorimetric method.

The values obtained are shown in Table IX.

Table IX: Soluble salts and free silica

	EC 25° μS/cm	Cl⁻ ppm	SO$_4^{2-}$ ppm	Free SiO$_2$ ppm
F-2	1512	200	294	379
F-17	1635	192	336	338
F-18	1557	193	303	320
F-37	1423	182	258	398
F-75	1579	203	309	316
F-102	1468	184	299	433
F-119	1412	200	200	486
AVERAGE	1512	193	286	381
STD. DEV.	83	8	44	63
A-1	1601	197	319	419
A-5	1557	193	303	408

A comparison with the values obtained during the last three years is established below (Table X), where it can be observed that chloride content for FEBEX clay is lower than for S-2 clay:

Table X: Comparison with values previously obtained

	EC 25° μS/cm	Cl⁻ ppm	SO$_4^{2-}$ ppm	Free SiO$_2$ ppm
PREVIOUS		249-433	232-391	159-433
FEBEX	1512 ± 83	193 ± 8	286 ± 44	381 ± 63

3.2.5 Cation exchange complex

Once the soluble salts were leached, the exchangeable cations of the clay were extracted by successive displacements with a tampon solution of 1M $AcONH_4$ pH 7 (Procedure 70-IMA-G-0-34) and determined by atomic emission spectroscopy, except K^+ that was determined by flame emission. The results obtained for every sample are shown in Table XI. All of the samples also present quantities of exchangeable Sr^{2+} (0.41 meq/100g), Ba^{2+} (0.02 meq/100g) and Mn^{2+} (0.06 meq/100g). Some of them contain exchangeable Al^{3+} in quantities less than 0.4 meq/100g.

Table XI: Exchangeable cations

Sample	Ca^{2+} meq/100g	Mg^{2+} meq/100g	Na^+ meq/100g	K^+ meq/100g	CEC meq/100g
F-2	47	39	26	2.3	114
F-17	48	37	25	2.3	113
F-18	44	37	25	2.2	108
F-37	55	41	26	2.2	124
F-75	47	35	23	2.2	108
F-102	52	36	25	2.3	116
F-119	48	35	25	2.3	110
AVERAGE	48	38	25	2.2	113
STD. DEV.	4	2	1	0.0	6
A-1	54	39	25	2.2	121
A-5	49	39	26	2.2	117

Although the relative proportion between cations remains the same, a certain difference has been observed with respect to previously determined values, for example the CEC for the FEBEX clay is higher than that of the clay from Serrata de Níjar tested during the last three years (S-2). A comparative Table is shown below:

Table XII: Comparison of exchangeable cations determined previously

	Ca^{2+} meq/100g	Mg^{2+} meq/100g	Na^+ meq/100g	K^+ meq/100g	CEC meq/100g
PREVIOUS	34-46	24-35	19-26	2-3	77-101
FEBEX	48 ± 4	38 ± 2	25 ± 1	2.2 ± 0.0	113 ± 6

3.3 Hydraulic properties

3.3.1 Hydraulic conductivity

Hydraulic conductivity has been determined on samples compacted with their initial water content to dry densities of 1.60 g/cm^3 and 1.70 g/cm^3. The clay is uniaxially compacted in cylindrical stainless steel rings, resulting in a block with a height of 2.5 cm and a diameter of 5 cm which is sandwiched between porous stones at the top and bottom. Water is injected at the top and bottom with a pressure of 0.6 MPa. Once the sample is saturated a hydraulic gradient is applied: the pressure is raised at the bottom to 5.2 MPa (for dry density 1.60 g/cm^3) or 7.2 MPa (for dry density 1.70 g/cm^3), giving a hydraulic gradient of

18400 and 25600, respectively. The outcoming water flow is measured with an electronic volume change apparatus as a function of time until stabilisation of the flow rate occurs. The hydraulic conductivity (K) is calculated by applying Darcy's law (Procedure 70-IMA-G-0-14). The final dry density and water content of the tested sample are determined at the end of the tests. The values obtained are shown in Table XIII.

Table XIII : Hydraulic conductivity values for different samples

Reference	Dry density g/cm^3	K m/s	Dry density g/cm^3	K m/s
F-2	1.59	3.1×10^{-14}	1.70	3.8×10^{-14}
F-18	1.60	5.9×10^{-14}	1.70	2.9×10^{-14}
F-37	1.60	6.0×10^{-14}	1.70	3.8×10^{-14}
F-75	1.61	5.9×10^{-14}	1.69	3.2×10^{-14}
F-109	1.59	6.4×10^{-14}	1.70	4.1×10^{-14}
F-119	1.58	8.3×10^{-14}	1.67	3.7×10^{-14}
AVERAGE	1.60	5.9×10^{-14}	1.69	3.6×10^{-14}
STD. DEV.	0.01	1.7×10^{-14}	0.01	4.4×10^{-15}

In Fig. 2 The values obtained for the samples analysed with dry density 1.6 and 1.7 g/cm^3 are plotted together with the fitting obtained previously for S-2 clay, that related hydraulic conductivity (K, m/s) to dry densities (ρ_d, g/cm^3) higher than 1.45 g/cm^3 through the logarithmic relationship (Villar & Rivas 1994):
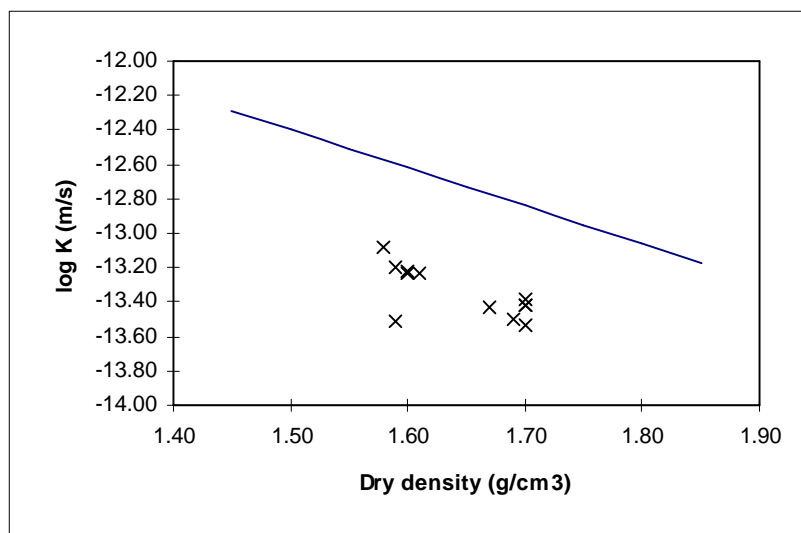
$$\log k = -2.2 \, \rho_d - 9.1$$

Fig. 2: Permeability values of the different samples analysed and fitting obtained previously for S-2 clay

The values obtained for the clay extracted for the FEBEX Project are lower than those obtained previously, specially for the dry density of 1.6 g/cm^3.

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3.3.2 Swelling pressure

Swelling pressure has been measured in samples of dry density 1.60 and 1.70 g/cm^3, following the Procedure 70-IMA-G-0-21. The clay is compacted uniaxially with its initial water content inside stainless steel rings of internal diameter 4.93 cm (for dry density 1.60 g/cm^3) or 3.57 cm (for dry density 1.70 g/cm^3). The height of the sample is 1.2 cm. The ring is placed in the oedometer cell where it is confined by porous plates and put in contact with water at the bottom. As the sample saturates the swelling is counteracted by loading the sample to avoid any deformation and maintain a constant volume. When stabilisation is reached, i.e. no deformation is observed for a given load during at least 24 hours, the sample is dismounted and the dry density and water content are checked. The swelling pressure is expressed as the effective load applied per unit surface.

Table XIV: Swelling pressures for dry densities 1.6 and 1.7 g/cm^3

Sample	Dd g/cm^3	Ps kg/cm^2	Dd g/cm^3	Ps kg/cm^2
F-2	1.59	>58	1.71	108
F-18	1.59	>62	1.70	83
	1.58	>50		
F-37	1.58	42	1.71	111
F-59	1.60	49		
F-65	1.58	>60		
F-75	1.60	30	1.70	77
	1.59	52	1.70	97
F-79	1.59	41		
F-93	1.59	36		
	1.59	>>56		
F-102	1.60	>56	1.69	105
F-109	1.57	52		
F-119	1.58	54	1.70	99
	1.60	52		
AVERAGE	1.59±0.01	50±9	1.70±0.01	97±13
A-1	1.61	32	1.72	85
	1.61	>68		
A-2	1.64	52		
A-3	1.62	54	1.72	124
A-4	1.62	56		
A-5	1.60	34	1.72	96
	1.62	48		
AVERAGE	1.62±0.01	48±13	1.72±0.00	102±20

The values obtained for the different samples analysed are plotted in Fig. 3 against dry density, together with the curve that relates swelling pressure (Ps, MPa) to dry density (ρ_d, g/cm^3) obtained previously for the clay S-2 (Villar & Rivas 1994):

$$\ln P_s = 5.9 \, \rho_d - 7.9$$

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The values obtained for the clay extracted for the FEBEX Project are in the range of those determined previously for the clay of the same quarry.
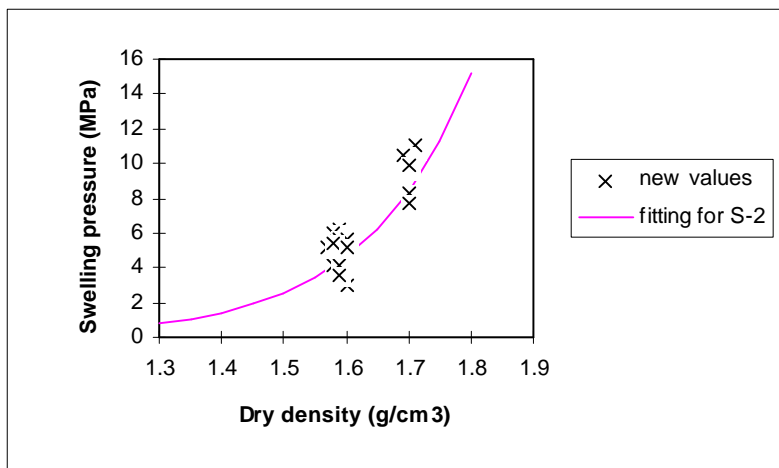

Fig. 3: Swelling pressure values for the different samples analysed and the curve fitted for S-2

3.3.3 Swelling under vertical load

The swelling developed under a given vertical load has been determined for the aliquots A-1 to A-5 of the homogenised sample 70-IMA-3-4-0. The procedure to prepare the sample is the same than that described in the previous section. The initial dry density of the samples is 1.6 g/cm^3 in all the cases. The samples are placed in the oedometer and a fixed vertical load is applied at the same time that the bottom of the sample is in contact with water to allow its saturation. The deformation is periodically registered until stabilisation occurs, which usually takes place 10 days after the beginning of the test. The percentage of swelling is calculated as the ratio of final deformation with respect to the initial height of the sample (12 mm). The values obtained are shown in Table XV.

Table XV: Swelling under vertical load for 70-IMA-3-4-0 clay

	vertical load 0.5 MPa		vertical load 0.9 MPa	
Reference	Initial Dd g/cm^3	swelling %	Initial Dd g/cm^3	swelling %
A-1	1.62	17.8		
A-2	1.60	17.2	1.59	15.9
A-3			1.61	14.7
A-4	1.62	17.8	1.59	13.4
A-5	1.62	17.2		
AVERAGE	1.61±0.01	17.5±0.3	1.60±0.01	14.7±1.3

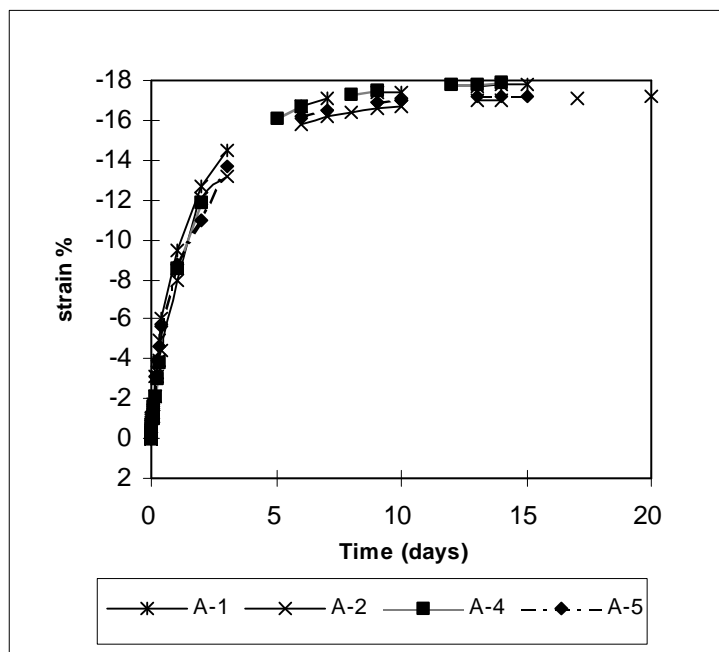The deformation vs. time for some of these tests is plotted in Fig. 4.

Fig. 4: Swelling vs. time of sample 70-IMA-3-4-0 under a vertical load of 0.5 MPa

3.3.4 Suction/water content relationship

The suction (s, MPa)/water content (w, %) relationship had been determined for S-2 clay for suctions under 14 MPa in membrane cells, and for suctions over 13 MPa in dessicators with sulphuric acid solutions. An experimental relationship, independent of the initial dry densities or water contents, was found (Villar et al. 1995):

$$w = 36.0 - 5.1 \ln (s) \quad r^2 = 0.953$$

For the natural water content of clay at laboratory conditions (11%) the suction value is 130 MPa. It has also been proven that this relationship is independent of particle grinding, as the same values have been found for the clay ground to a size less than 2 mm and less than 5 mm (Villar & Martín, 1996).

For checking purposes, three points of this curve have been determined in sulphuric acid dessicators for different samples of the FEBEX clay, following the Procedure 70-IMA-G-0-19. The suction points have been selected above, below and at the value corresponding to the natural water content, i.e. 260, 14 and 140 MPa.

Table XVI: Suction/water content relationship

Sample	initial w %	suction MPa	final ρ_d g/cm^3	final w %	final Sr %	w[1] %
F-2	14.8	255.5	1.65	9.0	39	7.7
F-17	16.0	255.5	1.61	9.0	36	7.7
F-37	13.3	255.5	1.63	9.1	38	7.7
F-59	13.3	255.5	1.63	9.2	38	7.7
F-75	11.7	260.6	1.62	8.3	34	7.6

Sample	initial w %	suction MPa	final ρ_d g/cm^3	final w %	final Sr %	w[1] %
AVERAGE	13.8±1.5	256.5±2.2	1.63±0.01	8.9±0.7	37±2	7.7±0.0
A-1	14.4	260.6	1.65	8.4	36	7.6
A-5	14.5	260.6	1.65	8.3	35	7.6
F-2	14.8	138.6	1.61	13.2	52	10.8
F-17	16.0	138.6	1.62	13.3	55	10.8
F-37	16.0	138.6	1.60	13.0	51	10.8
F-59	16.0	138.6	1.60	12.8	49	10.8
F-75	11.7	144.1	1.60	10.9	43	10.7
F-109	11.9	143.3	1.62	11.1	45	10.7
F-119	12.3	143.3	1.63	11.5	47	10.7
AVERAGE	14.9±1.8	139.7±2.3	1.61±0.02	12.3±1.0	49±4	10.8±0.1
A-1	14.4	144.1	1.63	11.7	48	10.7
A-5	14.5	144.1	1.62	11.6	48	10.7
70-IMA-3-4-0	13.1	143.3	1.62	11.5	47	10.7
F-109	11.9	126.6	1.60	12.1	48	11.3
F-119	12.3	126.6	1.59	12.7	49	11.3
70-IMA-3-4-0	13.1	126.6	1.60	12.3	48	11.3
F-2	14.8	14.5	1.39	22.7	65	22.4
F-17	16.0	14.5	1.43	22.6	69	22.4
F-37	13.3	14.5	1.35	22.6	61	22.4
F-59	12.7	14.5	1.36	22.8	62	22.4
F-75	11.7	14.0	1.35	21.9	59	22.5
F-109	11.9	14.9	1.35	21.9	59	22.2
F-119	12.3	14.9	1.35	22.2	60	22.2
AVERAGE	13.2±1.6	14.5±0.3	1.37±0.03	21.9±1.8	62±3	22.3±0.1
A-1	14.4	14.0	1.34	22.4	60	22.5
A-5	14.5	14.0	1.35	22.4	61	22.5
70-IMA-3-4-0	13.1	14.9	1.36	22.0	60	22.2

[1]according to the relationship previously established for S-2

In Fig. 5 the values obtained for the different samples are plotted together with the fitted line determined previously for S-2. A good agreement between former and new values can be observed, although for the higher suctions the water contents obtained are higher than those determined previously for S-2.
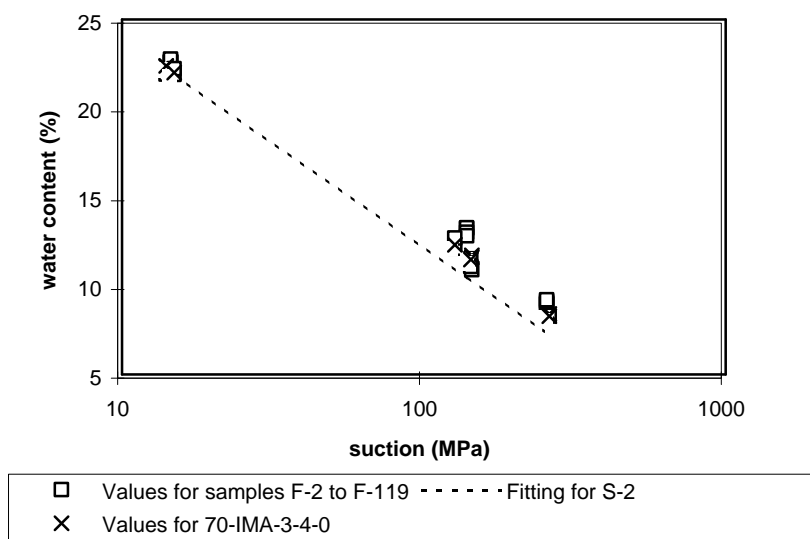
Fig. 5: Water content/suction relationship obtained for different samples

3.4 Thermal properties

The superficial thermal conductivity is measured with a probe placed on top of a compacted clay block, as described in Procedure 70-IMA-G-0-13. The blocks have been compacted uniaxially to dry densities of 1.6 and 1.7 g/cm^3 with water contents around 14 %, which correspond to saturation indexes (Sr) of 60%, and with water contents of 26 and 23%, which correspond to saturation indexes (Sr) of 100%. The compaction pressures have been around 14 MPa for the dry densities of 1.6 g/cm^3 and between 22 and 30 MPa for the dry densities of 1.7 g/cm^3. Afterwards, the blocks were dried at 100ºC during 24 hours, weighted and measured to verify the density change, and the thermal conductivity was measured again. 9 samples have been tested, and in all the cases the thermal conductivity has been measured by applying the probe on the compaction surface, i.e. the value obtained is the conductivity parallel to compaction.

The values obtained for dry densities of 1.6 and 1.7 g/cm^3 and different water contents are shown in Table XVII.

Table XVII: Thermal conductivity values (parallel to compaction) obtained in different samples

Sample	ρ_d g/cm^3	w %	Sr %	λ W/mK	ρ_d g/cm^3	w %	Sr %	λ W/mK
F-18	1.53	1.7	6	0.5013				
F-37	1.55	0.9	3	0.4797				
F-75					1.66	1.9	8	0.6195
F-75					1.67	0.1	0	0.6356
F-75					1.72	0.5	2	0.6293
F-109	1.53	0.1	0	0.4841				
F-18	1.60	1.0	4	0.5473				

Sample	ρ_d g/cm^3	w %	Sr %	λ W/mK	ρ_d g/cm^3	w %	Sr %	λ W/mK
F-37	1.60	2.0	8	0.5738				
F-109	1.58	0.1	0	0.4771				
F-119	1.59	1.1	4	0.5763				
F-2	1.59	15.5	60	0.6978	1.74	13.7	67	0.8992
F-18	1.60	15.5	61	0.7824	1.71	15.0	70	0.9402
F-37	1.63	12.6	52	0.7261	1.73	11.9	57	0.8339
F-75	1.60	13.1	51	0.6825	1.72	12.9	61	0.8077
F-102	1.59	15.4	60	0.6995				
F-119	1.60	13.3	52	0.6114	1.70	13.1	60	0.7923
F-2	1.62	26.0	105	1.2754	1.73	21.6	104	1.2183
F-17	1.63	25.3	104	1.2726	1.75	20.4	101	1.2450
F-37	1.62	26.2	106	1.3043	1.72	21.6	102	1.1247
F-59	1.64	25.4	106	1.3069	1.76	20.5	104	1.2342
F-75	1.61	25.8	103	1.3619	1.69	22.7	103	1.2717
F-79	1.61	27.1	108	1.2854	1.71	22.6	103	1.2541
F-102	1.59	27.4	106	1.2613	1.70	21.8	100	1.2709
F-119	1.60	26.6	104	1.2472	1.69	22.3	101	1.2531

In Fig. 6 the values of thermal conductivity (λ, W/mK) measured parallel to compaction of different samples, are plotted against water content (w, %). Straight lines have been fitted for the values corresponding to dry densities 1.6 and 1.7 g/cm^3 and are also plotted. The equation of these lines is:

For dry density 1.6 g/cm^3: $\lambda=0.4051+0.0314w$ ($r^2=0.8669$, 18 values)

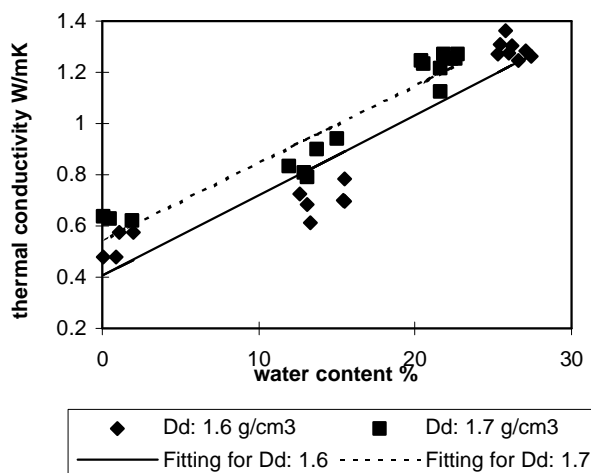For dry density 1.7 g/cm^3: $\lambda=0.5433+0.0302w$ ($r^2=0.9042$, 16 values)

Fig. 6: Thermal conductivity values vs. water content obtained for samples F-2 to F-119

The dispersion between the thermal conductivity values obtained for different samples is negligible, and allows the determination of an average value of thermal conductivity for the initial and final conditions of the clay barrier (Table XVIII):

Table XVIII: Thermal conductivity values of the clay barrier

	Initial	Final
Dry density (ρ_d, g/cm^3)	1.70	1.60
Water content (w, %)	14.0	25.5
Saturation index (Sr, %)	64	100
Thermal conductivity (λ, W/mK)	0.9661	1.2372

A good correlation has also been found between the saturation index (Sr, %) and the thermal conductivity (λ, W/mK). The values are plotted in Fig. 7, together with the fitted line, whose equation is:

$$\lambda = 0.463 + 0.007 Sr \quad (r^2 = 0.901, 37 \text{ values})$$
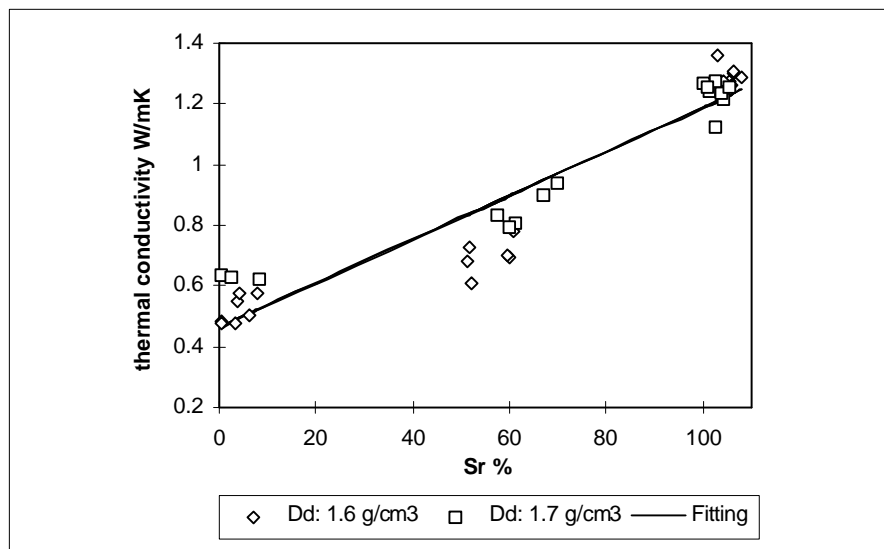
Fig. 7: Thermal conductivity vs. saturation index for samples F-2 to F-119

Thermal conductivity has also been measured in blocks of the clay 70-IMA-3-4-0 both parallel and perpendicular to compaction. The values obtained are shown in Table XIX and plotted in Fig. 8. The dissipation of heat through the barrier will mainly take place in radial sense, i.e., perpendicular to compaction. There is not an important variation of thermal conductivity in both directions, although it is always slightly higher when it is measured parallel to compaction.

Table XIX: Thermal conductivity values measured parallel and perpendicular to compaction for 70-IMA-3-4-0

Dd g/cm^3	w %	Sr %	λ parallel W/mK	λ perpend. W/mK
1.51	15	51	0.7621	0.7077

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Dd g/cm³	w %	Sr %	λ parallel W/mK	λ perpend. W/mK
1.58	15	57	0.8114	0.7283
1.63	15	62	0.955	0.8934
1.65	15	64	1.0003	0.894
1.69	15	68	0.9531	0.9525
1.52	20	70	0.9128	0.903
1.59	20	77	1.1187	0.993
1.65	20	85	1.1851	1.1622
1.67	20	88	1.1405	1.1686
1.72	20	95	1.4319	1.3918
1.52	25	87	1.0913	1.1517
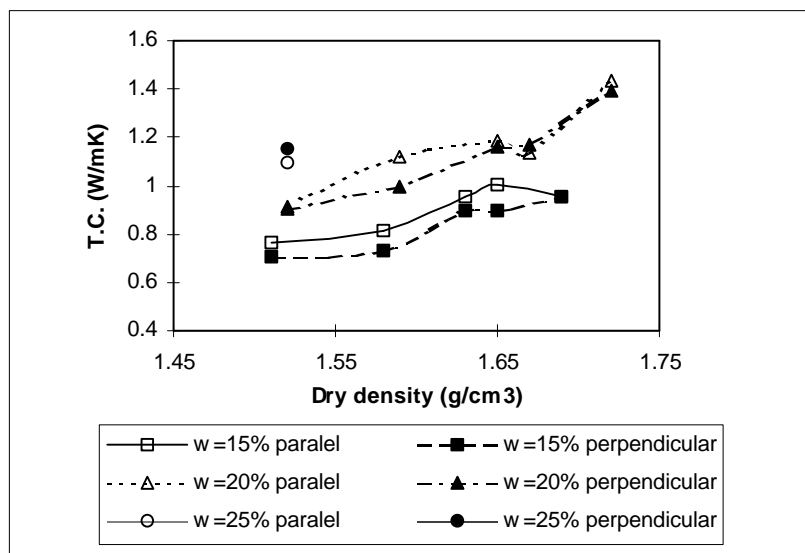
Fig. 8: Thermal conductivity measured in blocks of clay 70-IMA-3-4-0, parallel and perpendicular to compaction

A correlation has also been found with saturation index, and a straight line has been fitted to the values measured both perpendicular and parallel to compaction. It is plotted in Fig. 9, together with the line obtained for the samples F-2 to F-119 that was represented in Fig. 7.

◆ Paralel	■ Perpendicular
——— Fitting	——— Fitting for samples F-2 to F-119
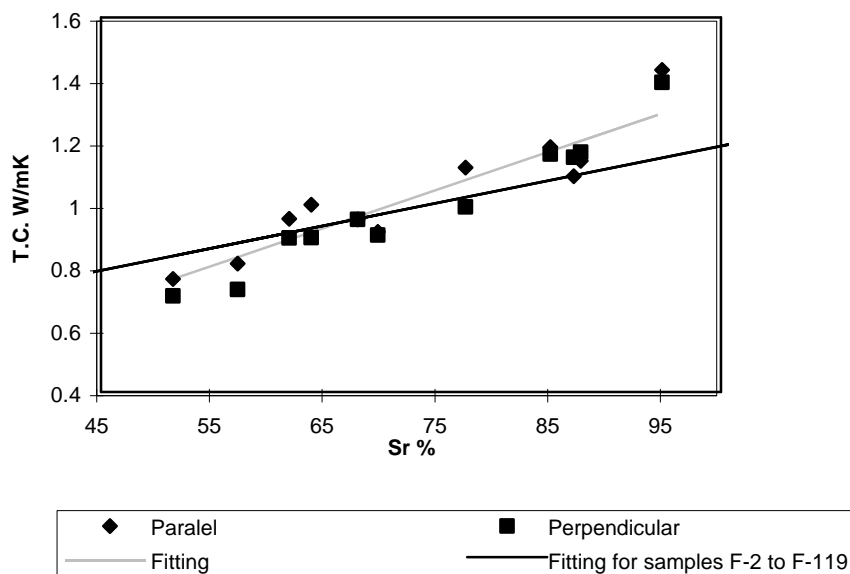
Fig. 9: Thermal conductivity vs. saturation index for clay 70-IMA-3-4-0

4. CONCLUSIONS

The clay extracted from the Serrata quarry for the FEBEX Project is an almost pure montmorillonite with high swelling capacity, low permeability, high adsorption properties (specific surface, liquid limit, cation exchange capacity and suction potential) and enough thermal conductivity.

With respect to the properties and characteristics considered, a good homogeneity has been observed between the different samples studied, i.e., through the whole processed lot.

The comparison of the results of this report with those previously obtained for clay S-2 extracted from the same quarry, show a slight variation in some of its characteristics:

- The mineralogy and chemistry basically remain the same, both for the bulk sample and the < 2 μm fraction. A lower content of Fe_2O_3 has been detected which would account for the lower specific weight of the new clay.

- Granulometric distribution and specific surface are similar.

- The soluble salts found are in a different proportion than in previous analyses, now being the SO_4^{2-} content greater than that of Cl^-.

- A higher content of free silica has been detected.

- The cation exchange capacity of the new clay is higher than that determined for S-2 clay, whereas the proportion between the different cations of the exchangeable complex remains the same: $Ca^{2+} > Mg^{2+} > Na^+ > K^+$.

- The hydraulic conductivity of the FEBEX clay is lower than that measured for S-2, specially for the dry density of 1.6 g/cm^3.

- The swelling pressures remain in the same order of magnitude.

- The suction/water content relationship remain the same.

- The thermal properties remain unchanged with respect to the S-2 clay.

The variations observed with respect to previous S-2 properties can be due partly to the extraction of most of the rock fragments during the processing of the clay for the FEBEX Project, which result in a reduction of permeability and an increase of swelling pressure.

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ANNEX I:

XRD AND DTA DIAGRAMS