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The study of Spanish clays for their use as sealing materials in nuclear waste repositories: 20 years of progress

El estudio de arcillas españolas para su utilización como material de sellado en almacenamientos de residuos radiactivos: 20 años de progreso

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Abstract

The paper summarises the studies that have been performed in Spain as regards the selection and characterisation of clays suitable for sealing and backfilling of radioactive waste repositories. This research began in the 80's under the auspices of ENRESA, the Spanish agency for nuclear waste management, and started by a survey of apt clay deposits and suppliers. The characterisation of the clays and the criteria followed for their further selection were those already accepted by the international community: mineralogical purity, retention properties, plasticity, low permeability, high swelling pressure and thermal conductivity. These initial studies resulted in the selection of deposits from the Cabo de Gata region (Almería) and the Tertiary Basin of Madrid (Toledo), whose detailed characterisation was carried out by several laboratories. The Cortijo de Archidona deposit (Almería) was finally selected and the bentonite taken there has been the object of various research projects that have ended in this bentonite being one of the best characterised from the mineralogical, thermal, hydraulic, mechanical, geochemical and alterability points of view. Besides, and more recently, the behaviour of the bentonite under the conditions of a repository has been studied at laboratory and natural scale, and the long-term evolution of the barrier is being analysed by natural analogues studies in the Cabo de Gata area.

Keywords: radioactive waste disposal, bentonite barrier, Spanish clays, montmorillonite, saponite, natural analogues.

Resumen

El artículo resume los estudios que se han llevado a cabo en España para la selección y caracterización de arcillas aptas como material de sellado y relleno en almacenamientos de residuos radiactivos. La investigación comenzó en los años 80 bajo el patrocinio de ENRESA, la agencia española para la gestión de residuos nucleares, con la búsqueda de yacimientos de arcilla apropiados. El tipo de caracterización realizado y los criterios seguidos para la selección estaban ya aceptados por la comunidad internacional: pureza mineralógica, propiedades de retención, plasticidad, baja permeabilidad, elevada presión de hinchamiento y conductividad térmica. Estos estudios iniciales dieron lugar a la selección de yacimientos de la región de Cabo de Gata (Almería) y de la Cuenca Terciaria de Madrid (Toledo), cuya caracterización detallada fue realizada por varios laboratorios. Finalmente se seleccionó el yacimiento de Cortijo de Archidona (Almería), y la bentonita procedente de él ha sido objeto de varios proyectos de investigación que han hecho que esta bentonita sea una de las más intensamente caracterizadas en sus aspectos mineralógico, térmico, hidráulico, mecánico, geoquímico y de alterabilidad. Además, posteriormente se ha estudiado el comportamiento de esta bentonita en condiciones similares a las de un almacenamiento a escala de laboratorio y natural, y la posible evolución a largo plazo de la barrera se ha analizado mediante estudios de análogos naturales en la región de Cabo de Gata.

Palabras clave: almacenamiento de residuos radiactivos, barrera de bentonita, arcillas españolas, montmorillonita, saponita, análogos naturales

1. Introduction

1.1. Deep geological disposal of high-level radioactive wastes

Radioactive wastes are considered to be any substance that contains or is contaminated with radionuclides in concentrations higher than those established by the competent authorities and for which no subsequent use is foreseen. Such wastes are produced during the generation of electricity using nuclear means, in the decommissioning of nuclear and radioactive installations and in the use of radioisotopes in industry, medicine, agriculture, research, etc. From the point of view of definitive disposal, radioactive wastes are generally classified into low and intermediate level wastes and high-level wastes. The latter have high specific short-lived emitter activities, contain appreciable concentrations of long-lived alpha-emitting radionuclides and are major heat producers.

The solution as regards protecting people and the environment against the radiations emitted by the radionuclides contained in high-level wastes consists in isolating them in such a way that throughout the period in which they remain active they cannot be released to the biosphere along any of the possible paths. The generally accepted option for the definitive disposal of high-level wastes (HLW) consists in their disposal in stable deep geological formations (500-1000 m) (Goguel *et al.,* 1987), as was suggested by the United States National Academy of Science in the 1950's. The safety of this disposal concept is based on the existence of a series of superimposed natural and artificial barriers to guarantee isolation (multibarrier concept): natural barriers, constituted by the host rock, and artificial barriers, constituted by the solid matrix of the waste itself, the metallic canister and its backfill, the sealing materials placed around the canister and the material backfilling the drifts of the installation.

Crystalline rocks (granite, basalt), clays and salts have been proposed as the surrounding geological material. The system of barriers aims to seal the possible escape paths for the radionuclides to the environment, the most important of which is the circulation of groundwater. In this context, the basic functions of the sealing material between the canister and the host rock are to prevent or limit the entry of water to the wastes and to contribute to radionuclide retention. Other additional functions are to contribute to heat dissipation and to provide mechanical protection for the waste canisters. In view of these functions, Pusch (1979) proposed the use of sodium bentonite (rocks made up of clay minerals and belonging to the smectites group, in which montmorillonite is the most common species) compacted in the form of high density blocks as sealing material, since it provides the following characteristics:

–Very low permeability, reducing the percolation of groundwater, since water transport is the main radionuclide transfer mechanism.

–High exchange capacity, and therefore a high capacity for ion adsorption in the event of radionuclide release.

–Sufficient thermal conductivity, to prevent the generation of excessive thermal gradients.

–Mechanical resistance to withstand the weight of the canister.

–Mechanical properties guaranteeing the homogeneous nature of the barrier, this including plastic behaviour to prevent the formation of fissures as a result of differential displacements or the location of stresses, and swelling potential favouring the self-sealing of existing voids.

Other material requirements of the barrier that have been underlined in subsequent research (Yong *et al.,* 1986) are as follows:

–Good compressibility, ensuring ease in processing, handling and transport to the disposal facility.

–Low shrinkage in response to the drying that will probably occur in the area surrounding the canister, in order to prevent the formation of a network of fissures.

–Non-excessive swelling pressure, to avoid damage to the system.

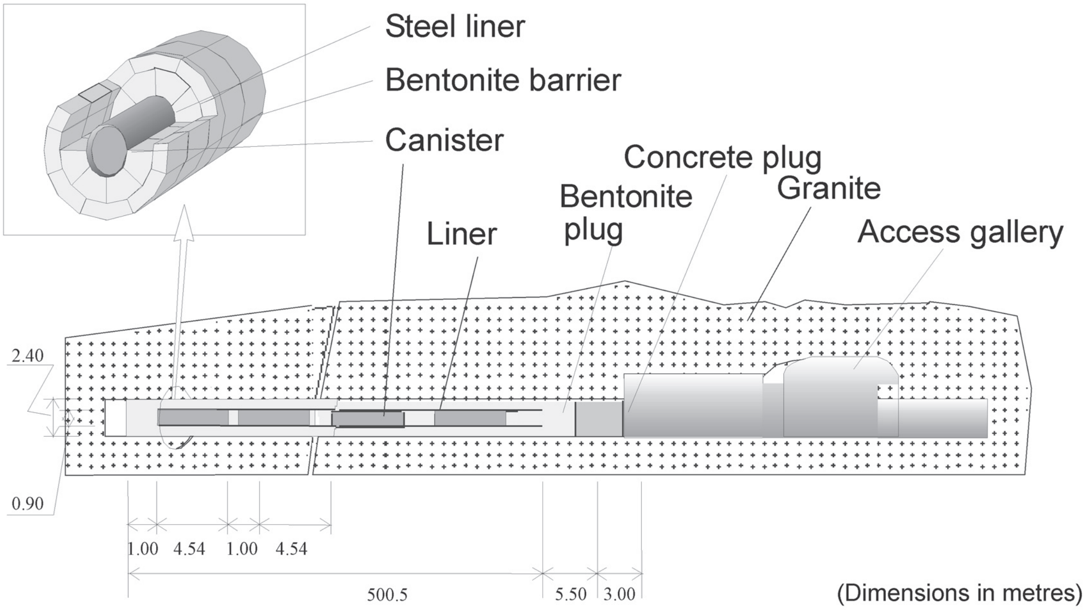

Fig. 1.- Longitudinal section of a disposal drift for the Spanish reference granite case (ENRESA, 1997).
Fig. 1.- Sección longitudinal de una galería de almacenamiento según el concepto español para granito (ENRESA, 1997).

–Suitable deformability, ensuring that the pressures generated by the rock massif and by the hydration of the expansive component of the barrier are absorbed and reduced by deformation of the barrier itself.

–Physical and chemical stability, ensuring the longevity of the system in relation to the conditions of the disposal facility, *i.e*. high temperatures, chemical gradients and the presence of vapour (Pusch and Gray, 1989; Güven, 1990).

Since the end of the 1980's, the agencies in charge of waste management in different countries have proposed other sealing materials, some based on the use of cement but most considering the use of bentonites, either non-sodic smectites or mixtures of expansive clay and aggregates in different proportions. As regards the aggregates, tests have been performed using crushed granite, crushed basalt, zeolites and quartz, quartz and graphite. The main objective of adding inert aggregates is to increase the thermal conductivity of the barrier, improve the mechanical resistance of the compacted blocks and reduce the cost of the material.

1.2. The Spanish case

The creation of ENRESA in 1984 marked the beginning of a new stage of research into the disposal of high-level radioactive wastes in Spain. In 1990, a series of activities was initiated with a view to defining a disposal system adequate for the Spanish case, within the framework of the deep geological disposal Project (Almacenamiento Geológico Profundo, AGP), the basic objective of which is to "avoid any type of radiological damage to mankind and his environment, using the waste concentration and confinement strategy". The geological formations considered are granite, clay and salt. The definitive disposal of the HLW is planned to be accomplished in canisters placed in the centre of the drifts of a disposal facility excavated at depth and surrounded by a sealing material, as shown in figure 1 for the granite case. The functions attributed to the sealing material surrounding the canister are those of reducing groundwater flows and the transport of corrosive substances, establishing a suitable physico-chemical environment around the canisters and providing mechanical protection against possible movements of the rock. Consequently, the properties to be provided by the sealing material are fundamentally low permeability and diffusivity, enough thermal conductivity, high sorption capacity and long-term stability (ENRESA, 1995).

The research relating to deep geological disposal covers from the determination of areas suitable for the installation of disposal facilities to the study of the behaviour of the fuel and canister, including site characterisation (structural, hydrogeological, geochemical, hydrogeochemical and radionuclide migration) and theoretical studies of engineered barriers.

In the AGP Project, consideration has been given to compacted bentonite as the canister sealing material in the case of saturated formations (clay and granite) and to a mixture of sand and clay materials as the backfilling material for the galleries and cavities. The dry density

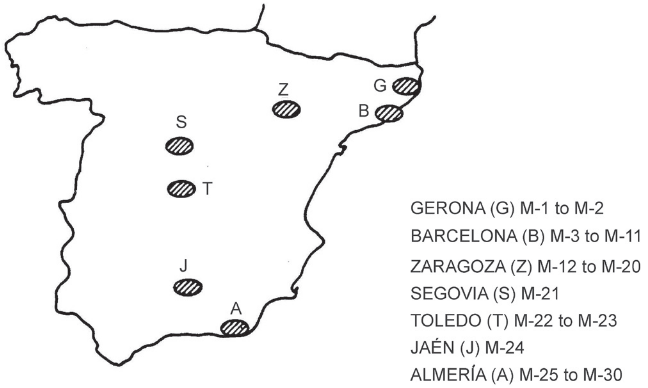

Fig. 2.- Location of clay suppliers (Mingarro *et al.,* 1991).

Fig. 2.- Localización de suministradores de arcilla (Mingarro *et al.,* 1991).

considered for the bentonite receptacle surrounding the canister is 1.65 g/cm^3. The layer of bentonite will measure 0.75 m in thickness and its temperature will not exceed 100 °C. A series of suitability studies led to a bentonite exploited in the province of Almería being selected as the reference sealing material. The following sections recapitulate on the prospecting, selection and study of the behaviour of materials suitable for the construction of engineered clay barriers in Spain, with a summary of the main results of each phase of the research.

2. The study of clay barriers in Spain: first stages

2.1. Prospecting and initial selection (1987-1989)

The study of backfilling and sealing materials began in Spain in 1987, with a Project financed by the European Community, performed by CIEMAT with participation of ENRESA (Mingarro *et al.,* 1991). This study had three objectives:

–To gain insight into the availability in Spain of clays suitable for use as backfilling and sealing materials.

–To study the possibility of using illitic clays as an alternative to smectitic clays, in order to minimise mineralogical unbalance with the granitic medium.

–To use ground granitic rock as an additive to the clay for backfilling material, this possibly reducing costs and contributing to the reconstitution of the environment of the disposal facility.

The prospecting of clay materials in Spain having been performed, study began on 30 samples from seven suppliers located in Gerona (samples 1 and 2), Barcelona (samples 3 to 11), Zaragoza (samples 12 to 20), Segovia (sample 21), Toledo (samples 22 and 23), Jaén (sample 24) and Almería (samples 25 to 30) (Fig. 2). An initial semi-quantitative determination of the mineralogy allowed 50 percent of the samples to be excluded because of their content of phyllosilicates being lower than 65 percent (Fig. 3). In accordance with the mineralogy of the fraction of less than 2 µm (Fig. 4), seven of these samples were selected; two were mainly made up of illite (samples 15 and 24) and the rest were smectites from the Cabo de Gata region (Almería) supplied by Minas de Gádor (samples 25, 26 and 28 to 30).

Finally, two bentonites were selected that had not been subjected to treatment in the factory: a bentonite known as "Serrata natural" (sample 26) from the Cortijo de Archidona deposit, in Almería, and an illite from Zaragoza (sample 15), these being chosen for their low carbonate and colloidal mineral content and high degree of plasticity and compressibility (Fig. 5). Analysis of the mechanical, hydraulic, thermal and physicochemical properties of both, and their behaviour when mixed with crushed granite and when heated, allowed the following conclusions to be drawn (Mingarro *et al.,* 1991):

–There are clays in Spain that might be used as backfilling and sealing materials.

–It is advisable to use smectitic clay and not illitic clay as a backfilling and sealing material, due to its greater swelling pressure, specific surface and cation exchange capacity (Fig. 6). The final dry density of the bentonite barrier should be above 1.6 g/cm^3 if montmorillonite is used and above 1.8 g/cm^3 if illite is used, in order to keep at adequate values its hydraulic and physico-mechanical properties.

–Crushed granite may be used as an additive to the smectite in the backfilling material, as long as it does not exceed 25 percent of the mixture. Above this percentage,

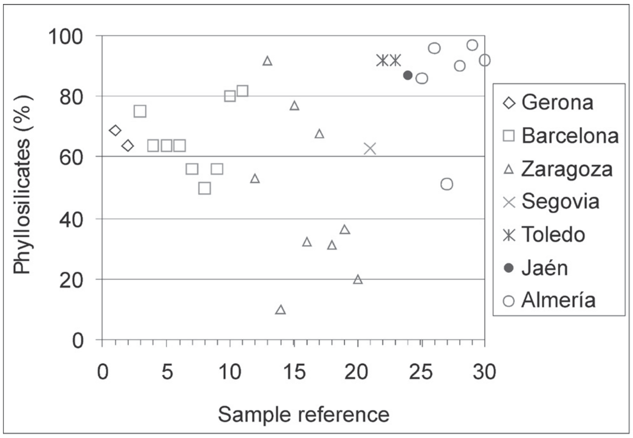

Fig. 3.- Weight percentage of phyllosilicates in the samples analysed (data from Mingarro *et al.,* 1991).

Fig. 3.- Porcentaje en peso de filosilicatos en las muestras analizadas (datos de Mingarro *et al.,* 1991).

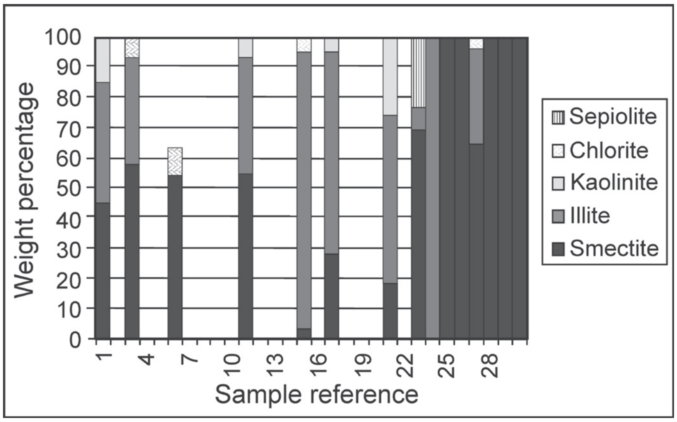

Fig. 4.- Mineralogical composition of the less than 2 µm fraction of the initially selected samples (data from Mingarro *et al.* 1991).

Fig. 4.- Composición mineralógica de la fracción menor de 2 µm de las muestras seleccionadas inicialmente (datos de Mingarro *et al.* 1991).

swelling pressure decreases (Fig. 7) and hydraulic conductivity increases (Fig. 8) out of the acceptable ranges.

–The heating of the clays at temperatures above 100°C negatively modify their properties, since it reduces their plasticity, swelling capacity, strength and specific surface area.

2.2. Study of two smectite-bearing areas

Parallel to the above, ENRESA promoted the study of two Spanish areas with important deposits of smectite clays that might be used as backfilling and sealing material for a future high-level radioactive waste disposal facility. These areas were the volcanic region of Cabo de Gata, in Almería, and the Tertiary Basin of Madrid in the province of Toledo. Three deposits were selected from each zone, these being considered as potential points of supply of the material in the future, because of the characteristics already known and the estimated reserves.

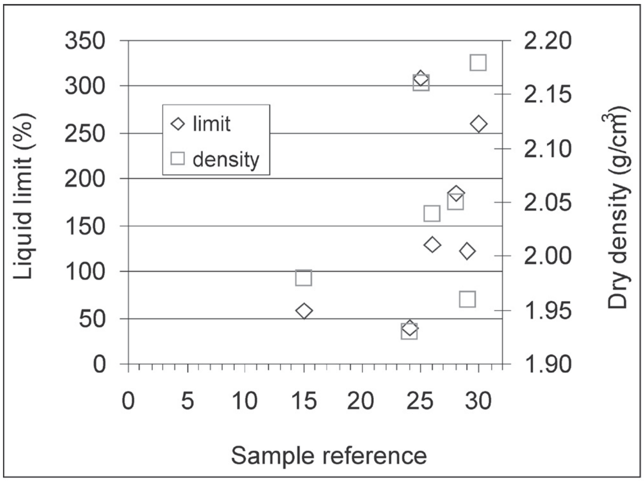

Fig. 5.- Plasticity (expressed as liquid limit) and compressibility (expressed as dry density after uniaxial compaction at 123 MPa of the clay with hygroscopic water content) of the initially selected samples (samples 15 and 24 are illites, the rest, smectites) (data from Mingarro *et al.,* 1991).

Fig. 5.- Plasticidad (expresada como límite líquido) y compresibilidad (expresada como densidad seca tras compactación uniaxial a 123 MPa de la arcilla con su humedad higroscópica) de las muestras seleccionadas inicialmente (las muestras 15 y 24 son illitas, el resto esmectitas) (datos de Mingarro *et al.,* 1991).

CSIC-Zaidín performed a preliminary characterization of 30 bentonite outcrops (10 samples per outcrop) in the Cabo de Gata region, that allowed the selection of the three deposits (Cortijo de Archidona, in the Serrata de Níjar, Morrón de Mateo, in the Rambla de los Escullos and Los Trancos, in the northern area of the Sierra de Gata) for a comparative study. These deposits were selected on the basis of the following criteria: the smectite content should be higher than 70-75 percent and the minimum estimated reserves should be in the order of 10^6 tons. The bentonites from Cortijo de Archidona are very pure and have outstanding colloidal properties, the Los Trancos deposit –also of a great purity– have the major bentonite reserves, and the bentonites from Morrón de Mateo have important quantities of sand, what could avoid the addition of additives (Linares *et al.,* 1993). The average mineralogical composition of the bentonites from the selected deposits is shown in Table 1 and the structural formulae of the smectites in Table 2.

The UAM group studied, in a first step, the mineralogical and physicochemical properties of 28 samples taken from three clay quarries located in the Tertiary Basin of Madrid: the Cerro del Águila-Cerro del Monte deposit

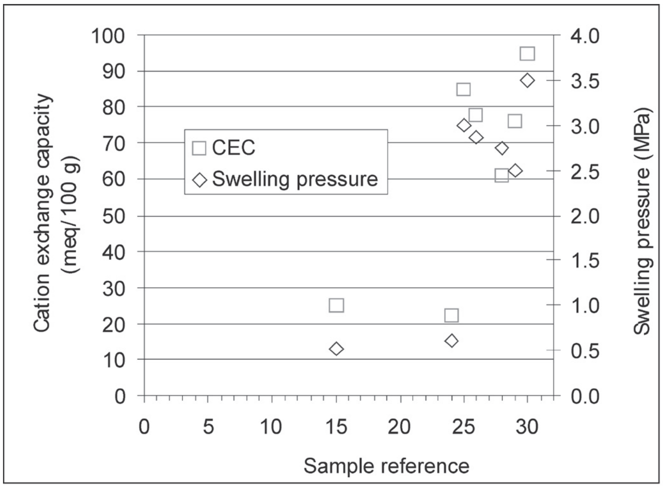

Fig. 6.- Cationic exchange capacity and swelling pressure of the initially selected samples (samples 15 and 24 are illites, the rest, smectites) (data from Mingarro *et al.,* 1991).

Fig. 6.- Capacidad de cambio catiónico y presión de hinchamiento de las muestras seleccionadas inicialmente (las muestras 15 y 24 son illitas, el resto esmectitas) (datos de Mingarro *et al.,* 1991).

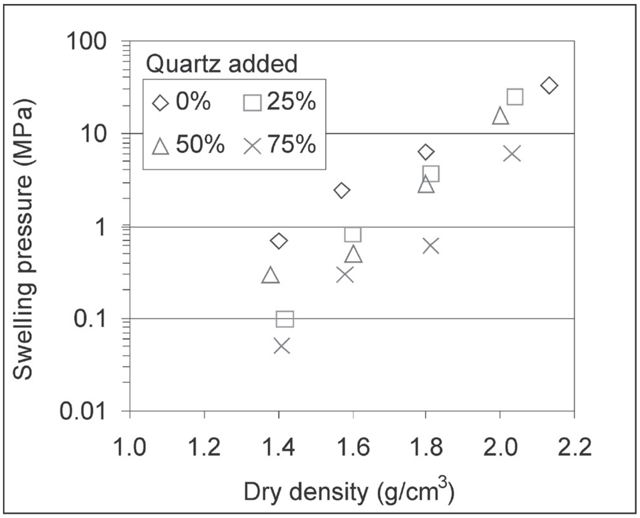

Fig. 7.- Swelling pressure of montmorillonite (sample 26) / quartz mixtures (data from Mingarro *et al.,* 1991).

Fig. 7.- Presión de hinchamiento de mezclas de montmorillonita (muestra 26) y cuarzo (datos de Mingarro *et al.,* 1991).

(green clays at Villaluenga de la Sagra), the Santa Bárbara deposit (pink clays at Esquivias) and the Yuncos deposit (brown clays at Yuncos) (Cuevas, 1992). Table 3 shows some properties of these clays and their comparison with some limit values established at the beginning of the research. It is remarkable the unusual swelling pressure developed by some clays. The physicochemical and mechanical properties of the Madrid Basin clays were in agreement with their particular crystal-chemical nature. In fact, they are composed of smectites of the saponite-stevensite group (Mg-smectites). Moreover, green clays were of saponitic nature (Al-substituted tetrahedral-charged), what is very rare in the sedimentary environment in which they formed (Table 4).

CIEMAT received two samples from each selected deposit –each weighing 200 kg– to study the granulometric distribution and specific gravity, mineralogy and geochemistry, Atterberg limits and total and external specific surface. Dynamic and static compaction tests were also performed. The superficial thermal conductivity was determined using compacted samples. The results obtained are to be found in Rivas *et al.* (1991), Villar and Dardaine (1990) and Pérez del Villar (1989a, b), and some of them are shown in Table 5.

On the basis of the results obtained by the laboratories, one deposit was selected from each zone, the Cortijo de Archidona at Cabo de Gata, made up mainly of montmorillonite type smectites, and the Cerro del Águila-Cerro del Monte deposit in the Tertiary Basin of Madrid, which is fundamentally constituted of saponite, accompanied by varying proportions of illite and sepiolite. The criteria taken into account in making the selection were those indicative of the suitability of the material for use as a HLW disposal facility backfill and sealing material: mineralogical purity, high specific surface, high liquid limit, high proportion of size fraction of less than 2 µm, high thermal conductivity and good compressibility, the latter being an additional requirement for the manufacturing of high density blocks. This aspect can be checked in figure 9 for the samples from Toledo and in figure 10 for the samples from Almería (Rivas *et al.,* 1991): for a given compaction energy (modified Proctor), the densities reached by the samples of Cerro del Águila (MCA in figure 9) and Cortijo de Archidona (S in figure 10) are the highest.

2.3. Selection of one deposit (1989-1991)

Using the two selected reference clays, S-2 (Cortijo de Archidona in the Serrata de Níjar, Almería) and MCA-C (Cerro del Águila-Cerro del Monte, in the province of Toledo), the characterisation of their physicochemical properties and alterability was detailed. For this purpose, a 5000-kg sample from each deposit was used, dried at 60°C to water content of close to 10 percent and factory ground to a size of less than 5 mm. For use in the laboratory, the samples were ground to less than 2 mm (except in those cases in which the aim was to determine the effect of granulometry on a given property), and were stabilised at laboratory temperature and humidity conditions (18-25°C, 50-60 percent relative humidity). A part of the prepared sample was sent to the CSIC-Zaidín (S-2), UAM (MCA-C) and CEA (Commissariat à l'Énergie Atomique, France) laboratories.

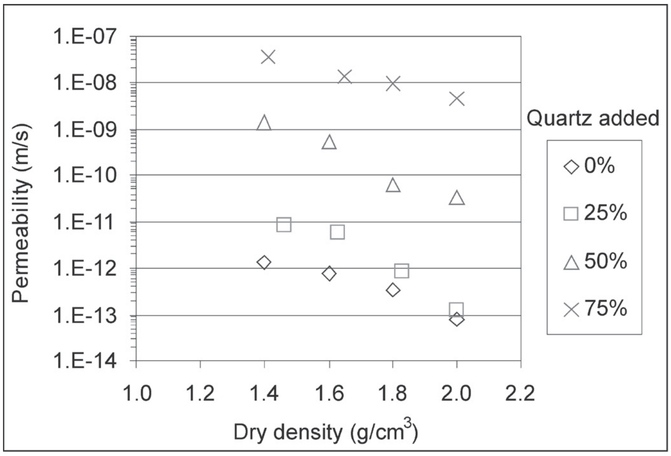

Fig. 8.- Hydraulic conductivity of montmorillonite (sample 26) / quartz mixtures (data from Mingarro *et al.,* 1991).

Fig. 8.- Conductividad hidráulica de mezclas de montmorillonita (muestra 26) y cuarzo (datos de Mingarro *et al.,* 1991).

Mineral (%)	Los Trancos	Cortijo de Archidona	Morrón de Mateo [1]
Smectite	97±2	92±4	72±11
Cristobalite	1±1	2±1	6±4
Quartz	1±1	2±1	3±2
Plagioclase	7±1	3±1	9±4
Calcite	Traces	2±2	4±4
Biotite	Traces	1±1	Traces

[1] Also different quantities of pyroxenes, amphiboles, K-feldspars, zeolites and pyrolusite

Table 1.- Average mineralogical composition of the bentonites from the deposits selected in the Almería area (CSIC-Zaidín, Linares *et al.,* 1993).

Tabla 1.- Composición mineralógica media de las bentonitas de los depósitos seleccionados en el área de Almería (CSIC-Zaidín, Linares *et al.,* 1993).

The characterisation performed at CIEMAT included tests for the determination of different parameters and of the influence on different properties of the dry density and water content of the sample, the temperature of the determination, the maximum grain size used, the addition of quartz sand in different proportions and the preheating of the clay to different temperatures. The following studies were carried out on both clays:

– Dynamic compaction study by manual and semi-automatic beating in an axial press: determination of water contents and pressures necessary to reach particular dry densities, and the influence on final density of granulometry and of the addition of quartz sand in different proportions.

– Unconfined compressive strength: the influence of sample dry density and water content, of the granulometry used and of the addition of different proportions of quartz sand.

– Free swelling.

– Swelling pressure: analysis of the influence of dry density and of the proportion of quartz sand.

– Saturated hydraulic conductivity for different dry densities, proportions of quartz sand and measurement temperatures.

– Thermal conductivity: analysis of the influence of dry density, water content and the proportion of quartz sand.

– Oedometric tests: study of clay consolidation.

– Triaxial tests.

– Ion diffusion study: determination of distribution coefficients for ^{137}Cs and ^{60}Co.

– Determination of adsorption-desorption isotherms.

– Study of hydrothermal alterability: influence of treatment time, temperature and KCl concentration.

The Atterberg limits, swelling pressure, unconfined compressive strength and hydraulic conductivity were also determined for samples subjected previously to heating at 100, 200 and 300°C (Fig. 11). Also determined were the modifications caused by heating as regards mineralogy, specific gravity, specific external surface and microstructure observed through electron microscopy.

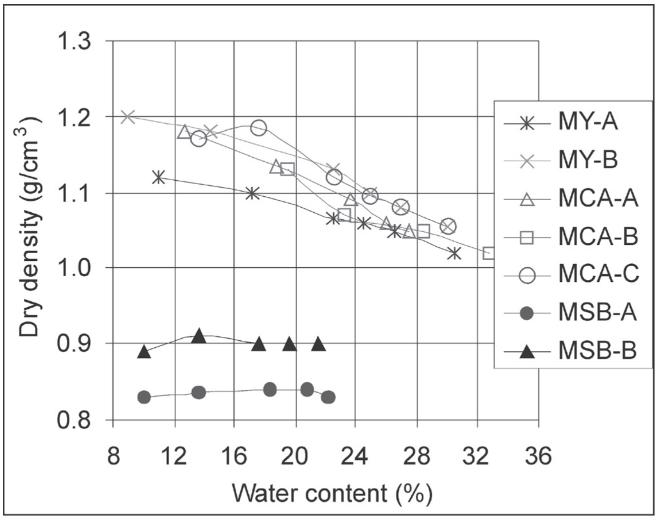

Fig. 9.- Results of compaction tests (Modified Proctor UNE103501: 1994) on samples from Toledo area (MY: Yuncos; MCA: Cerro del Águila; MSB: Santa Bárbara) (Rivas *et al.,* 1991).

Fig. 9.- Resultados de ensayos de compactación (Proctor modificado UNE103501:1994) en muestras del área de Toledo (MY: Yuncos; MCA: Cerro del Águila; MSB: Santa Bárbara) (Rivas *et al.,* 1991).

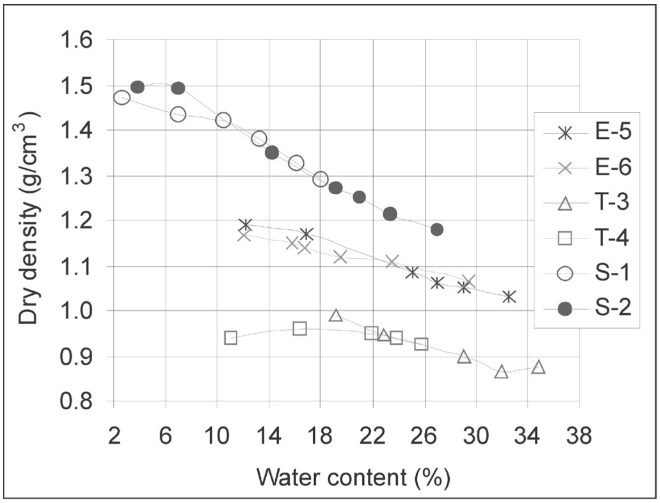

Fig. 10.- Results of compaction tests (Modified Proctor UNE103501: 1994) on samples from Almería area (E: Morrón de Mateo; T: Los Trancos; S: Cortijo de Archidona) (Rivas *et al.,* 1991).

Fig. 10.- Resultados de ensayos de compactación (Proctor modificado UNE103501:1994) en muestras del área de Almería (E: Morrón de Mateo; T: Los Trancos; S: Cortijo de Archidona) (Rivas *et al.,* 1991).

Deposit	Si_{IV}^{4+}	Al_{IV}^{3+}	Al_{VI}^{3+}	Fe_{VI}^{3+}	Mg_{VI}^{2+}	X^{+}	X_{VI}	Σ_{VI}
Los Trancos	7.74	0.26	2.93	0.24	0.84	0.85	0.58	4.12
C. Archidona	7.78	0.22	2.78	0.33	1.03	0.82	0.59	4.15
Morrón de Mateo	7.61	0.38	2.57	0.51	1.10	0.91	0.52	4.19

Table 2.- Structural formulae calculated on a $O_{20}(OH)_4$ basis of the smectites from the deposits selected in the Almería area (CSIC-Zaidín, Linares *et al.,* 1993).

Tabla 2.- Fórmula estructural calculada sobre $O_{20}(OH)_4$ de las esmectitas a partir de los depósitos seleccionados en el área de Almería (CSIC-Zaidín, Linares *et al.,* 1993).

		Cerro del Águila			Santa Bárbara			Yuncos		
Parameter	**Limit value**	**Max**	**Min**	**Avg**	**Max**	**Min**	**Avg**	**Max**	**Min**	**Avg**
Fraction size <2ì m (%)	> 80	98	85	93	93	76	85	96	79	88
Smectite content (%)	> 60	96	58	82	kerolite-stevensite			86	69	81
Amorphous content (%)	< 1									
SiO_2		0.4	0.1	0.2	0.4	0.1	0.2	0.1	0.04	0.06
Fe_2O_3		--	--	--	0.04	0.02	0.03	0.23	0.07	0.14
Al_2O_3		--	--	--	--	--	--	--	--	--
CEC (mmol/kg)	> 60	112	53	77	57	38	49	86	59	73
Organic matter (%)	<0.2	0.09	0.04	0.07	0.58	0.27	0.37	0.11	0.05	0.09
$CaCO_3$ (%)	< 6	--	--	--	0.3	--	0.1	8.0	6.0	5.0
CEC (meq/100g)				77			49			73
Specific surface BET (m^2/g)				155			257			12
Swelling pressure[1](MPa)				6			12			4

[1] For dry density of 1.4 g/cm^3

Table 3.- Properties of clays from the Madrid Basin (Max: maximum value, Min: minimum value, Avg: average value) and limit values of these properties established for sealing and backfilling purposes (Cuevas *et al.,* 1993).

Tabla 3.- Propiedades de las arcillas de la Cuenca de Madrid (Max: valor máximo, Min: valor mínimo, Avg: valor medio) y valores límite establecidos de estas propiedades, para arcillas con propósitos de relleno y sellado (Cuevas *et al.,* 1993).

In addition, hydrothermal alteration experiments were conducted by CSIC on the montmorillonite and by UAM on the saponite. The objective of these studies was to test the stability of each type of clay under heating up to 175ºC in an aqueous solution environment dominated by KCl salts (0.01-0.5 M). The main reactivity response expected was the adsorption of K^+ cations in the interlayer space of the smectite and, subsequently, its dehydration. This process, together with some crystal-chemical rearrangements, is the illitization reaction, in which the interlayer space collapses due to dehydration and causes the loss of many of the useful properties of smectites (swelling, water retention, cation adsorption).

In the case of the montmorillonite from Cabo de Gata, the potassium ionic exchange was the only process observed, and no other changes were detected in the bentonites after the hydrothermal treatment (Linares *et al.,* 1992, 1993). The saponite from the Madrid Basin was stable up to 175ºC, showing no sign of illitization or crystallochemical changes (Cuevas *et al.,* 1992, 1994). The high hydrothermal stability of saponite had been previously reported by Whitney (1983).

These studies complemented the results obtained at CIEMAT (Rivas *et al.,* 1991; Pérez del Villar *et al.,* 1991; Villar and Dardaine, 1990), and allowed the montmorillonite from the Cortijo de Archidona deposit, reference S-2, to be definitively selected, mostly for its better compaction properties, although both clays (montmorillonites and saponites) in fact fulfilled the requirements for use as a barrier material. Good compressibility was taken

Deposit	Si_{IV}^{4+}	Al_{IV}^{3+}	Al_{VI}^{3+}	Fe_{VI}^{3+}	Mg_{VI}^{2+}	Ti_{VI}^{4+}	CH0	Σ_{VI}	Ca^{2+}	K^{+}
Cerro del Águila	7.26	0.74	0.52	0.33	4.56	0.04	-0.16	5.47	0.39	0.12
Santa Bárbara	7.69	0.31	0.09	0.07	5.62	0.00	-0.28	5.78	0.29	0.01
Yuncos	7.75	0.25	0.43	0.20	4.80	0.02	-0.42	5.46	0.30	0.07

Table 4.- Structural formulae calculated on a $O_{20}(OH)_4$ basis of smectites from the deposits selected in the Madrid Basin (Cuevas *et al.,* 1993).

Tabla 4.- Fórmula estructural calculada sobre una base de $O_{20}(OH)_4$ de esmectitas a partir de depósitos seleccionados en la Cuenca de Madrid (Cuevas *et al.,* 1993).

Reference[1]	Phyllosilicates -%-	Liquid limit -%-	Specific surface[2] -m^2/g-	Hygroscopic water content -%-	Dry density[3] -g/cm^3-	Thermal conductivity -W/m·K-
MY-A	82	220	304	16.1	1.58	0.87
MY-B	84	133	212	13.1	1.79	1.07
MCA-A	90	237	216	16.1	1.66	0.87
MCA-B	90	129	385	15.8	1.78	1.11
MCA-C	91	188	336	15.5	1.79	1.07
MSB-A	91	153	223	16.0	1.65	1.01
MSB-B	94	137	150	17.0	1.64	0.99
E-5	74	122	341	18.6	1.72	1.03
E-6	66	85	332	13.3	1.78	1.11
T-3	95	97	198	20.6	1.64	1.15
T-4	98	90	152	19.5	1.64	1.15
S-1	96	139	553	19.0	1.73	1.24
S-2	86	213	517	15.8	1.82	1.21

[1] MY: Yuncos, MCA: Cerro del Águila-Cerro del Monte, MSB: Santa Bárbara, E: Morrón de Mateo, T: Los Trancos, S: Cortijo de Archidona

[2] Methylene blue method

[3] After uniaxial compaction at 100 MPa with hygroscopic water content

Table 5.- Physical properties of samples from Almería and Toledo areas.

Tabla 5.- Propiedades físicas de las muestras de las áreas de Almería y Toledo.

as selection criterion because it is a key property for the manufacturing of blocks, which is an essential aspect of the installation of the barrier. The conclusions drawn during this phase were as follows:

– Both uniaxial and dynamic compression were adequate for the production of high density compacted blocks.

– The grain size distribution did not modify the final density of the blocks.

– Saturated hydraulic conductivity and swelling pressure depend on the dry density of the clay (ρ_d), in accordance with an exponential relation. A dry density of 1.60 g/cm^3 satisfies the hydraulic requirements of the barrier.

– The hydraulic conductivity of the clay increases with temperature, this increase possibly being explained in terms of reduction of the kinetic viscosity of the water.

– The thermal conductivity of the material increases with dry density and water content.

– The addition of quartz sand did not imply any major improvement in the properties of the material. Although many properties of the bentonite (hydraulic conductivity, swelling capacity, thermal conductivity) improve with the increase of dry density (see above), and the addition of quartz increases the density of the manufactured blocks for a given compaction energy, it was seen that most of the properties of the bentonite/sand mixtures depend actually on the clay dry density, the quartz acting just as an inert material (Villar and Rivas, 1994). Figure 12 shows how the thermal conductivity of blocks of a given dry density does not increase with the addition of quartz.

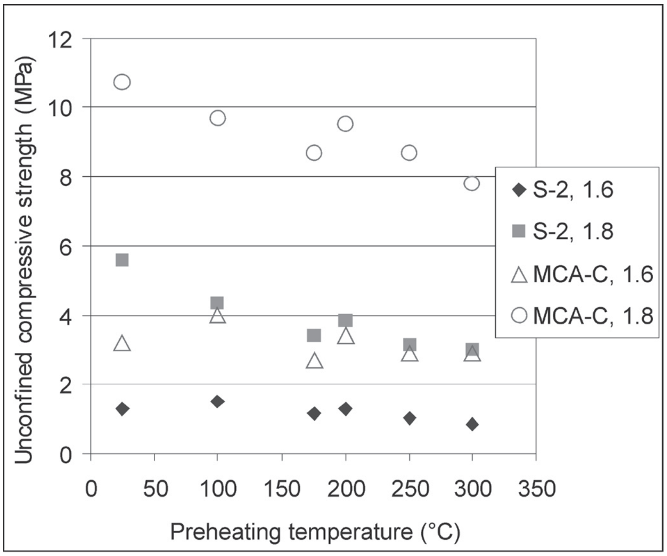

Fig. 11.- Unconfined compressive strength of specimens obtained by uniaxial compression of the bentonite with 10 percent water content (dry density indicated in g/cm^3) (data from Rivas *et al.,* 1991).

Fig. 11.- Resistencia a la compresión simple de muestras obtenidas por compresión uniaxial de la bentonita con humedad del 10 % (densidad seca indicada en g/cm^3) (datos de Rivas *et al.,* 1991).

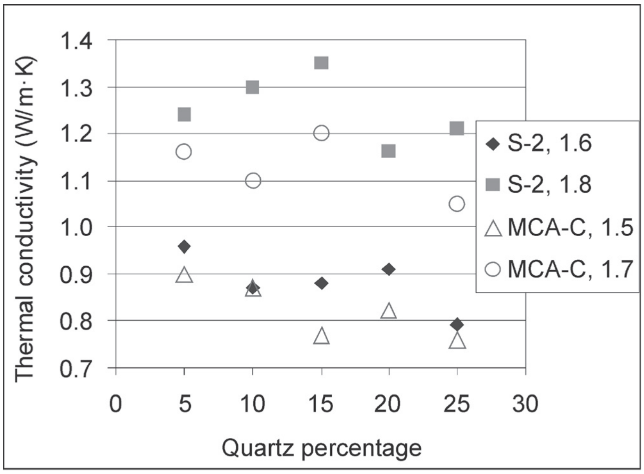

Fig. 12.- Thermal conductivity of bentonite/quartz mixtures for samples S-2 and MCA-C (dry density indicated in g/cm^3) (data from Rivas *et al.,* 1991).

Fig. 12.- Conductividad térmica de mezclas bentonita/cuarzo para las muestras S-2 y MCA-C (densidad seca indicada en g/cm^3) (datos de Rivas *et al.,* 1991).

Simultaneously, industrial type uniaxial compaction tests were performed on both clays under a contract with CEA (Martín and Dardaine, 1990; Martín *et al.,* 1990). Also carried out was a clay barrier validation test in a vertical shaft, performed at the Fanay-Silord mine (France) using the S-2 clay (Astudillo *et al.,* 1993). Figure 13 shows the final arrangement of blocks of compacted bentonite before their installation at the vertical shaft. The vertical disposal was one of the concepts considered at that moment.

2.4. Detailed studies on bentonite S-2 (1991-1995)

2.4.1. Thermo-hydro-mechanical and geochemical behaviour studies

The second phase of characterisation of the S-2 clay from the Cortijo de Archidona deposit began in 1991. For these studies, 24 t of bentonite were used, supplied by Minas de Gádor in October 1990 and prepared at its Almería plant by drying at 60°C and grinding to a size of less than 5 mm. This material was further ground to less than 2 mm for use in the laboratories.

This phase included characterisation of the properties and behaviour of the material under the conditions to which it would be subjected once emplaced in the disposal facility, *i.e.* when subjected to simultaneous heating and hydration on opposing fronts over long periods of time. For this, the effects caused by thermo-hydraulic flux in compacted blocks and the hydro-mechanical behaviour of the material in unsaturated conditions were studied (Villar, 1995a).

The first issue was addressed by means of tests consisting basically in subjecting cylindrical blocks of compacted clay, confined in hermetically sealed and non-deformable cells, to simultaneous heating and/or hydration on opposing fronts. The dimensions of the clay blocks used for these tests were between 8 and 14 cm in length and between 3 and 15 cm in diameter. Figure 14 shows the main components of a thermo-hydraulic test, with the cell in the central part.

This research provided information about the temperature field inside the clay, the variables affecting water intake, the water content and dry density distribution inside the clay, the chemical and physical changes occurred

Fig. 13.- Arrangement of compacted bentonite blocks to be placed in an experimental vertical shaft (Astudillo *et al.,* 1993).

Fig. 13.- Disposición de bloques de bentonita compactada preparados para su instalación en un pozo experimental vertical (Astudillo *et al.,* 1993).

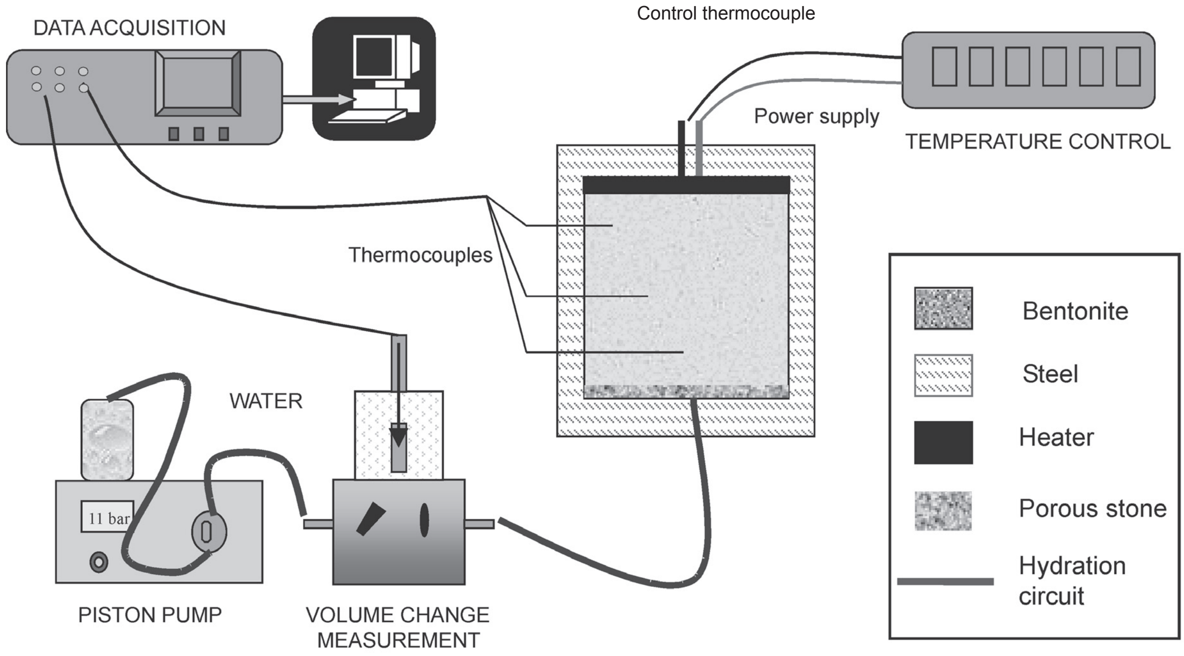

Fig. 14.- Schematic diagram of assembly for the performance of laboratory thermo-hydraulic test.
Fig. 14.- Disposición de elementos para realización de ensayos de laboratorio en celdas termo-hidráulicas.

(changes in cationic exchange capacity, salinity, specific surface), the generation and evolution of saline fronts and the variation of hydro-mechanical properties of the bentonite (Villar *et al.,* 1996, 1997).

Furthermore, study of the material in the unsaturated state focussed on determination of the free volume suction/water content relation of the clay with different values of water content and density, and on the performance of oedometric tests with controlled suction. The results obtained show a hardening of the bentonite due to the effects of suction and the repercussion of the vertical load applied during hydration of the sample on the reversibility of the strain induced (Villar, 1995b; Villar and Martín, 1996).

Likewise, the characterisation of the clay continued, with new aspects being addressed, such as the determination of porosimetry distribution and of the specific heat depending on temperature. New determinations of specific gravity, cation exchange capacity and exchangeable cations, thermal conductivity, etc. were undertaken. Other issues addressed for the first time were extraction and analysis of the interstitial water and bacteriological analysis (Villar *et al.,* 1997; Cuevas *et al.,* 1997).

2.4.2. Hydrothermal alteration studies

For its part, during the period 1992-1995, CSIC-Zaidín carried out a study of the hydrothermal alteration of bentonites in potassium solutions (Linares *et al.,* 1996). This investigation was focused on the mineralogical stability of smectite to assess its conversion to illite under repository conditions. This reaction requires potassium fixation in the smectite interlayer space and reorganisation of the smectite structure into the illite one. Potassium, temperature and time favour the reaction. The smectite fraction (<20 μm) of S-2 samples was treated with potassium solutions (0.025-1 KCl mol/L) at 60-200ºC for 1 day to 1 year. The analysis of the equilibrium solutions and the characterisation of the final products allowed monitoring the chemical and mineralogical changes undergone by the smectite.

The potassium fixation in the interlayer space of the natural smectite occurs only in solutions concentrated in potassium, which is not the situation in granite formations. On the other hand, a kinetic equation was derived for the smectite-to-illite conversion and different scenarios were considered to determine the evolution of the bentonite mineralogy. For extreme temperature conditions (120ºC) and 10^{-5} mol/L in K^+ (granite solution), after 10.000 years the amount of bentonite remaining in the bentonite is higher than 60 percent (Fig. 15), which is sufficient to maintain the bentonite properties. This conclusion reveals that this bentonite is mineralogically stable enough under repository conditions.

Although saponitic clays from the Madrid Basin had been discarded as reference materials for their worst compressibility, a complementing study was carried out by the UAM group financed by ENRESA in parallel to the detailed study developed by CSIC on the montmorillonitic clay. MCA-C sample was hydrothermally treated for 30 to 365-day periods with granitic groundwater solutions at temperatures of 45 to 200ºC. The material, containing traces of sepiolite and illite, transformed into a mono-mineral saponitic clay at 125-200ºC. The time for conversion was estimated between 20 and 7 years for temperatures of 45 and 200ºC, respectively. In addition to the establishment of a simple kinetic law for the reaction conversion (Cuevas *et al.,* 1998), microstructural (SEM-TEM) and surface changes were also studied (Cuevas *et al.,* 2001). In general, the mineralogical and textural changes observed at temperatures below 125ºC were of minor importance. It can be concluded that this type of clays would be suitable in alkaline environments imposed by the presence of concrete in some disposal concepts, since saponitic clays are thermodynamically stable in alkaline solutions.

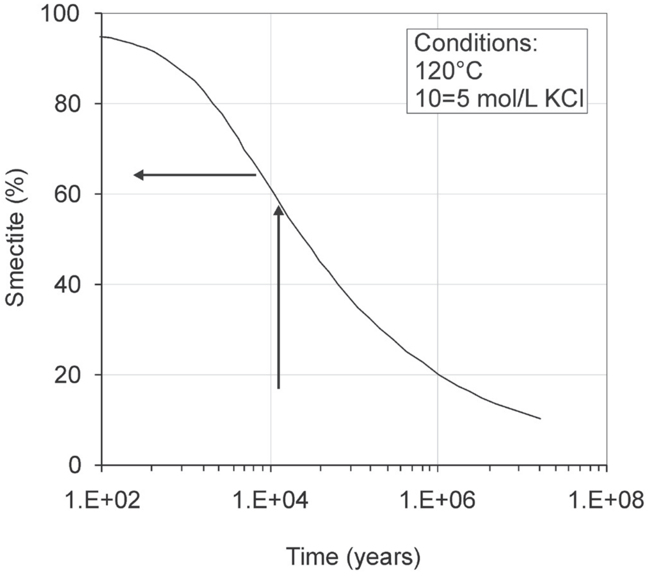

Fig. 15.- Modelling of the conversion of smectite into illite according to $(1/S^{(n-1)} - (1/S_o^{(n-1)} = (n-1)\cdot k\cdot K^{m.t}$, where S_o (0.96) and S are the original and final concentration of smectite, n (5), k ($7.6\cdot10^{-6}$) and m (1/4) are constants, K is the potassium concentration (0.00001 mol/L) and t is time (years) (Cuadros and Linares, 1996).

Fig. 15.- Modelización de la conversión de esmectita en illita según $(1/S^{(n-1)} - (1/S_o^{(n-1)} = (n-1)\cdot k\cdot K^{m.t}$, donde S_o (0.96) y S son las concentraciones iniciales y finales de esmectita, n (5), k ($7.6\cdot10^{-6}$) y m (1/4) son constantes, K es la concentración de potasio (0.00001 mol/L) y t es el tiempo (años) (Cuadros y Linares, 1996).

3. Studies of the bentonite as engineered barrier

3.1. Study of the clay under repository conditions: The FEBEX Project

In the R+D plans performed prior to 1994, which have been partially summarised above, ENRESA studied sources of supply of the materials to be used in the clay barrier, along with its thermal, hydraulic, mechanical and geochemical behaviour. Likewise, integral characterisation studies were performed on granitic massifs. The next step in gaining insight into the feasibility of the AGP concept, and with a view to making progress regarding understanding and evaluation of the near-field behaviour, was the performance of a large-scale experiment, the FEBEX Project (ENRESA, 2000). The purpose of the FEBEX Project was the study of the near-field components of a high-level radioactive waste disposal facility in crystalline rock, in accordance with the Spanish concept (Fig. 1), in which the waste canisters are placed horizontally in galleries, surrounded by a clay barrier made up of high density compacted bentonite blocks (ENRESA, 1995). More specifically, three objectives were mapped out: 1) demonstration of the feasibility of handling and constructing a system of engineered barriers; 2) study of thermo-hydro-mechanical (THM) processes in the near field; and 3) study of thermo-hydro-geochemical (THG) processes in the near field.

The FEBEX Project, coordinated by ENRESA –assisted by NAGRA (Switzerland) in certain aspects– and co-funded by the European Commission, has included the participation of numerous European organisations and has been developed in two phases: FEBEX I, from 1994 to 1998, and FEBEX II, from 1999 to 2004. The Project consisted of three main parts: an *in situ* test under natural conditions and at full scale; a test on an almost full-scale mock-up; and a series of laboratory tests aimed at providing information complementary to the two large-scale tests. All these activities served as a support for a far-reaching programme of modelling work (ENRESA, 2000).

In the two large-scale tests, the thermal effect of the wastes is simulated by means of heaters, while hydration is natural in the *in situ* test and controlled in the one performed on the mock-up. Both tests are monitored, this allowing the evolution of the temperature, total pressure, water content, water pressure, displacements and other parameters to be obtained continuously in different parts of the barrier and the host rock, this information being used to check the predictions of the thermo-hydro-mechanical and geochemical models. The *in situ* test is performed in a gallery excavated in the granite of the underground laboratory managed by NAGRA at Grimsel (Switzerland), whereas the mock-up test is being performed at the CIEMAT installations (Madrid). Figure 16 illustrates the process of assembling the bentonite blocks for the mock-up test.

The laboratory tests included characterisation tests and tests for the acquisition of parameters, as well as THM and THG tests, the objective of which is to measure the changes undergone by the bentonite in response to actions analogous to those taking place in the clay barrier and their repercussion on subsequent behaviour. In addition, these tests provide support for the THM and THG modelling, serving to check its predictive capacity. The results obtained in laboratory tests can be found in Villar *et al.* (1998), ENRESA (2000), Villar (2000, 2002), Fernández (2003), Missana *et al.* (2004) and Lloret *et al.* (2004). On the THM side, they refer to 1) the study of the behaviour of the bentonite under high suction and pressure variations, 2) the water retention capacity of the clay, 3) the effect of temperature and salinity on the hydro-mechanical properties, 4) the influence of the hydraulic gradient on permeability. On the THG side, the studies concern 1) the pore water in the bentonite barrier, 2) the geochemical processes taking place at the bentonite/aqueous solution interface, 3) the processes of sorption and transport of radionuclides in the bentonite.

The clay used for all the Project experiments, both the large-scale and laboratory tests –the FEBEX clay–, comes from the Cortijo de Archidona deposit (Almería), the same from which the S-2 bentonite was taken five years before. A bentonite deposit, even though very homogeneous, has horizontal as well as vertical variations. For a project such as FEBEX, it was important to use material as homogeneous as possible and determine its properties so as to reduce the uncertainties in the subsequent modelisations and the final interpretation of the results of the entire experiment. However, for a performance assessment of a repository, it is necessary to know the range of the relevant properties of a massive source of supply of bentonite. Thus, the comparison with the information and data sets gathered in previous research phases is very useful.

3.2. Study of the long-term evolution of the bentonite engineered barrier: natural analogues

Given that numerous laboratory studies were performed on bentonite properties as candidate material for the engineered barrier, it seemed reasonable to start in 1997 the study of natural analogues from appropriate bentonite deposits, in order to increase our knowledge about the long-term thermo-hydraulic-mechanical-chemical evolution of the buffer material (Barra I project). A natural analogue offers the possibility to study how nature behaves both under different conditions and over different periods of time. Analogues are very useful in helping to understand the phenomena that can occur over long spans of time. For that, a series of bentonite deposit in the Cabo de Gata region (Almería) –from where the reference clay comes– were selected and studied by CIEMAT, CSIC, Enviros, QuantiSci and ENRESA. These bentonite deposits were Pozo Usero, Morrón de Mateo, Cala de Tomate, El Toril, San José, El Corralete, Cala Rajá, Curva de Felipe y Cortijo de Archidona (Fig. 17), which were classified, according to the analogue processes expected, as follows: Cala de Tomate and Morrón de Mateo for the temperature effect, Pozo Usero for pressure effect, El Corralete, Cala Rajá and El Toril for the effect of the intrusion of oxidant water, and Cortijo de Archidona, El Corralete y San José for the effect of the intrusion of high salinity water (Arcos *et al.,* 2001).

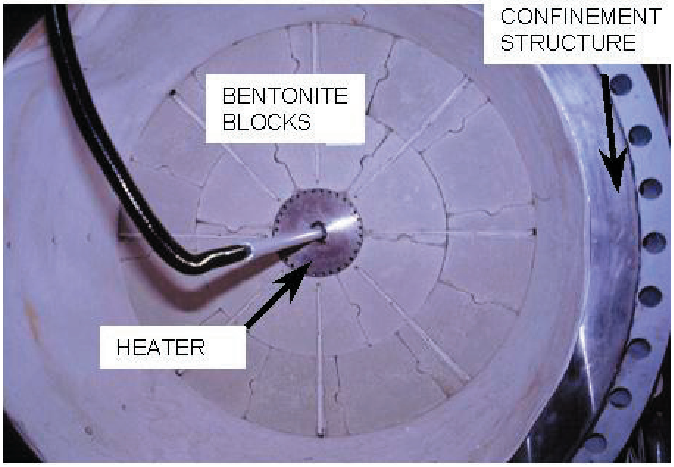

Fig. 16.- Appearance of one section of bentonite blocks with the heater inserted in the mock-up test (Martín, 2004).

Fig. 16.- Aspecto de una sección de bloques de bentonita con el calentador insertado en el ensayo en maqueta (Martín, 2004).

The results obtained (Pelayo *et al.,* 2000; Arcos *et al.,* 2001) during the first phase of the project advised to reduce the number of bentonite deposits considered, as well as the analogue processes to be studied during the second phase of the project (Barra II project). Thus, the deposits and processes selected and studied were Morrón de Mateo for the thermal effect and Cala de Tomate and Cortijo de Archidona for the saline effect. The results, reported in Arcos *et al.* (2004), Pérez del Villar *et al.* (2005a, b), Fernández (2003) and Fernández *et al.* (2005), are summarised below.

The thermal effect induced by the Morrón de Mateo volcanic dome on the adjacent bentonitised tuffaceous beds was studied as a natural analogue of the thermal behaviour of the bentonite engineered barrier. This investigation was focussed on the detection of the chemical differences between smectites from proximal and distal (El Murciano area) zones to the dome, as well as to test

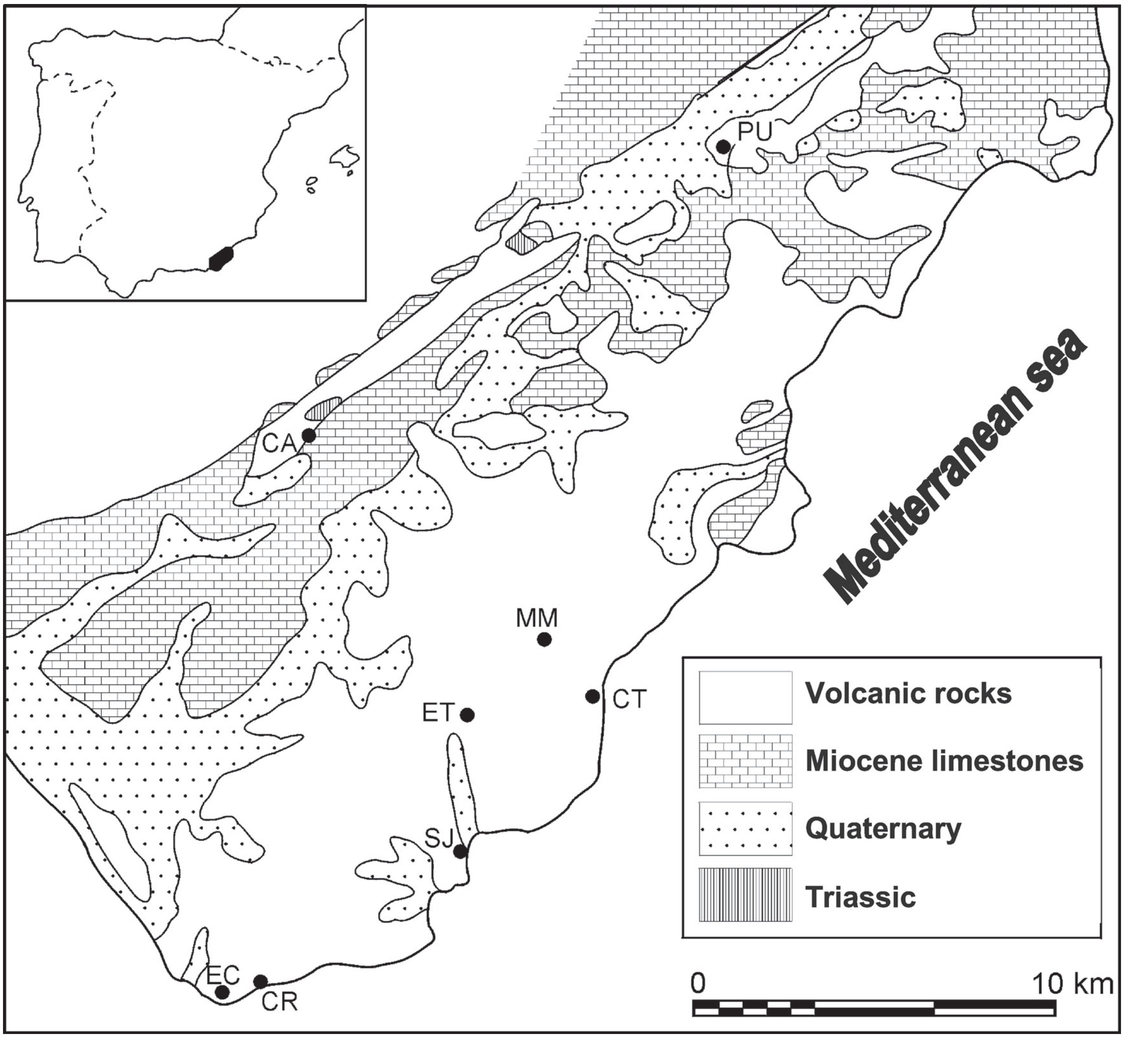

Fig. 17.- Geological map of the Cabo de Gata region, showing the bentonite deposits selected for natural analogue studies: PU: Pozo Usero, MM: Morrón de Mateo, CT: Cala del Tomate, ET: El Toril, SJ: San José, EC: El Corralote, CR: Cala Rajá, CA: Cortijo de Archidona (Caballero *et al.,* 1985).

Fig. 17.- Mapa geológico de la región de Cabo de Gata, con localización de los yacimientos de bentonita seleccionados para estudio como análogos naturales: PU: Pozo Usero, MM: Morrón de Mateo, CT: Cala del Tomate, ET: El Toril, SJ: San José, EC: El Corralote, CR: Cala Rajá, CA: Cortijo de Archidona (Caballero *et al.,* 1985).

whether the temperatures calculated based on the oxygen and hydrogen isotopic values (Delgado, 1993) correspond to their formation or transformation (Fig. 18, Fig. 19).

The initial hypothesis was that the chosen smectites could be formed under marine conditions, being later transformed and isotopically re-equilibrated with hot fluids in the vicinity of the intrusion. To check this hypothesis, a detailed mineralogical, chemical, geochemical and isotopic study was performed on the smectitised tuffaceous materials and the overlaying biocalcarenites outcropping near and far from the dome. The results show that distal smectites are dioctahedral Al-smectites, similar to those from other deposits in the region, whereas proximal smectites are dioctahedral Fe and Mg-rich smectites (except in just one proximal sample in which both di- and trioctahedral smectites coexist), showing two evolutionary trends on a Fe-Mg-Al ternary diagram (Fig. 20a). Similar features are observed when their structural formulae are plotted on the muscovite-celadonite-pyrophylite diagram (Fig. 20b). Thus, they plot in the smectite domain with interlayer charge less than 1, which is mainly due to octahedral substitution for distal smectites, whereas for proximal ones is caused by both octahedral and tetrahedral substitutions. In this ternary diagram, the domains of both proximal and distal smectites are partially overlapped. Further, proximal biocalcarenites are enriched in Fe-rich dolomite in relation to the distal ones.

The $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ values in carbonates and δD in smectites indicate equilibrium with seawater. In contrast,

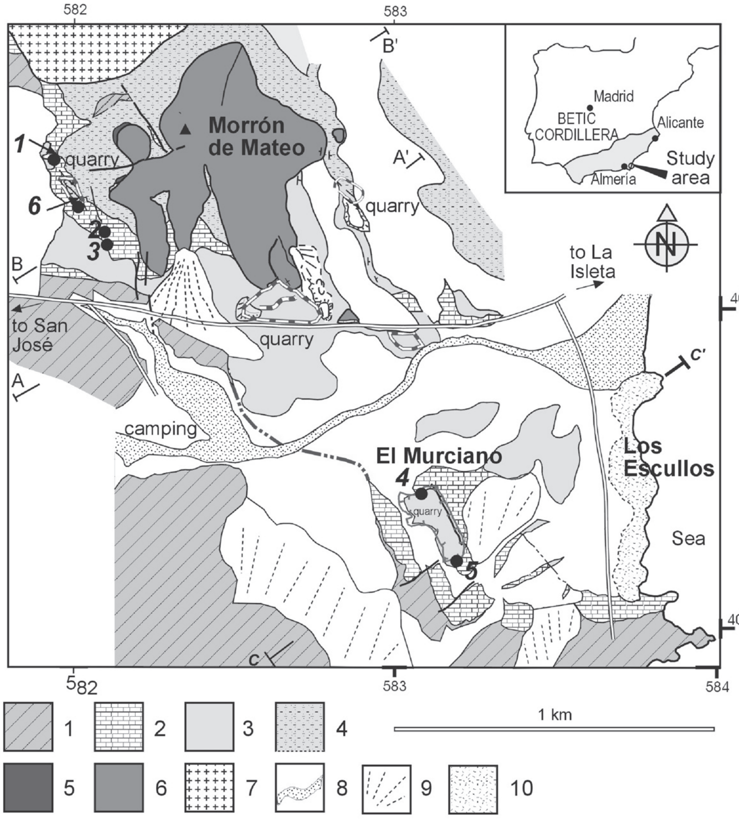

Fig. 18.- Geological map of the studied area, showing the location of sampled profiles (modified after Fernández-Soler, 2002). 1: hornblende andesite breccias and lavas; 2: Tortonian marine sedimentary rocks (limestones, calcarenites, conglomerates and sandstones); 3: layered tuffs; 4: grey tuffs; 5: white dacitic pyroclastic tuffs; 6: the Morrón de Mateo dacite dome; 7: Rodalquilar Complex (rhyo) dacitic rocks; 8: undifferentiated Quaternary sediments; 9: alluvial fans; 10: Pleistocene oolitic sandstones (fossil beach).

Fig. 18.- Mapa geológico de la zona estudiada, con indicación de los perfiles de muestreo (modificado de Fernández-Soler, 2002). 1: hornblenda, andesita, brechas y lavas; 2: sedimentos marinos tortonienses (calizas, calcarenitas, conglomerados y areniscas); 3: tobas estratificadas; 4: tobas grises; 5: tobas dacíticas piroclásticas blancas; 6: domo dacítico de Morrón de Mateo; 7: Complejo Rodalquilar de rocas (rio)-dacíticas; 8: sedimentos cuaternarios indiferenciados; 9: abanicos aluviales; 10: areniscas oolíticas del Pleistoceno (playa fósil).

$\delta^{18}O$ values of carbonates and smectites indicate that these minerals were transformed and re-equilibrated between 40 and 90ºC, and between 55 and 66ºC, respectively, independently of their location with respect to the dome.

These data suggest that the transformation of calcite into Mg-Fe-carbonates and the occurrence of Fe- and Mg-rich smectites close to the dome resulted from a chemically induced process at similar temperatures and, at least, under transitional redox conditions. The compositional differences among samples suggest that Fe, Mg and minor Mn were supplied by a probable contaminant front originating from the dome, migrating through the sediments and becoming more diluted away from the source. The absence of a well-defined thermal gradient in the system could be due to the small size, semi-closed and shallow character of the basin, as well as to its high underlying volcanic activity.

From a physicochemical point of view, no significant differences in the total exchange cations and BET specific surface area values are observed in relation to the crystallochemical differences observed between proximal and distal smectites.

As we have seen above, the candidate bentonite to build the bentonite-engineered barrier is an Al-smectite similar to that of the distal zone (El Murciano area) of the Morrón de Mateo volcanic dome (Astudillo, 2001). Furthermore, the thermal peak induced by radioactive decay of the nuclear spent fuel after burial, estimated to reach 100ºC, is another important physical variable of the engineered system, since this parameter will have a large influence on the hydration state of the bentonite barrier. This temperature is also similar to that calculated for the studied natural system.

After sealing of a deep geological repository, it is expected that the steel container will be affected by two corrosion phases. The first will occur immediately post-closure, under aerobic conditions, and as a result of the oxidation by the air occluded in the bentonite barrier. These effects will be weak and restrictive in space. In contrast, during the second phase, which will start when the barrier is totally saturated (approximately 10^3-10^4 years), the oxidation of the steel container will occur, resulting in the formation of both magnetite (Fe_3O_4) and Fe-oxyhydroxides or siderite ($FeCO_3$), depending on the physicochemical conditions in the system and the production of hydrogen. In any case, the probable coexistence of Fe(II) and Fe(III) indicates that transitional redox conditions can prevail in the engineered system.

With respect to the natural system all these physicochemical conditions were met as a result of the volcanic dome intrusion. So, relatively high temperature, Fe(II)-Fe(III) concentration, total hydration of the smectitised tuffaceous bed and transitional redox conditions worked all together close to the Morrón de Mateo volcanic dome.

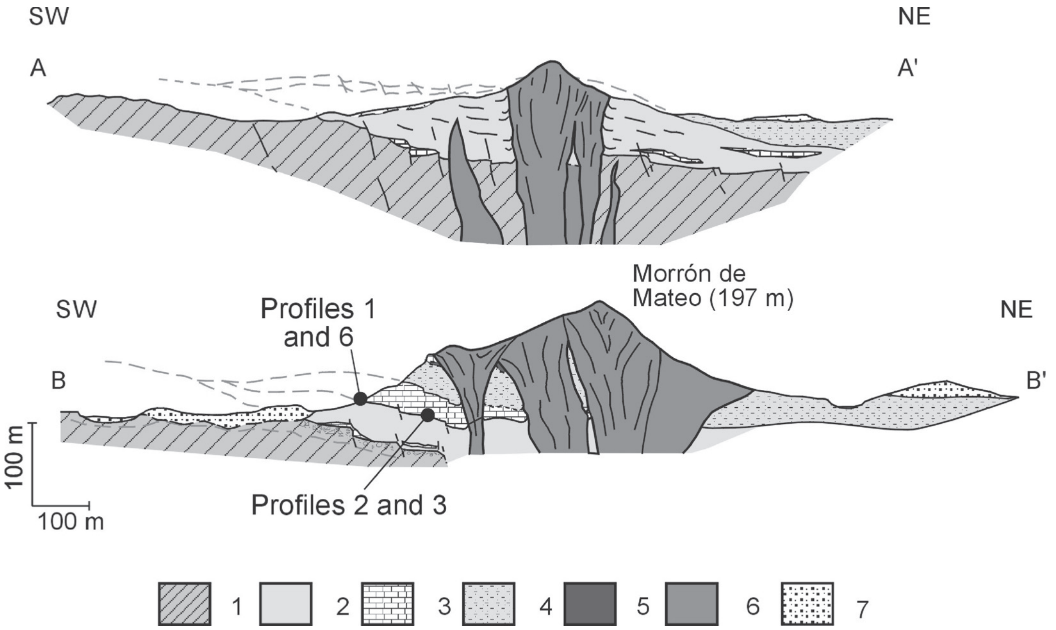

Fig. 19.- Illustrative cross-sections A-A´ and B-B´ (see location in figure 18) through the Morrón de Mateo sequence, showing the intrusive relation between the Morrón de Mateo dome and the volcano-sedimentary sequence (Fernández-Soler, 2002). 1: hornblende andesite breccias and lavas; 2: layered tuffs; 3: Tortonian marine sedimentary rocks (limestones, calcarenites, conglomerates and sandstones); 4: grey tuffs; 5: white dacitic pyroclastic tuffs; 6: the Morrón de Mateo dome; 7: recent alluvial sediments.

Fig. 19.- Cortes A-A´ y B-B´ (localización en figura 18) a través de la secuencia de Morrón de Mateo, con indicación de la relación intrusiva entre el domo de Morrón de Mateo y la secuencia volcano-sedimentaria (Fernández-Soler, 2002). 1: hornblenda, andesita, brechas y lavas; 2: tobas estratificadas; 3: sedimentos marinos tortonienses (calizas, calcarenitas, conglomerados y areniscas); 4: tobas grises; 5: tobas dacíticas piroclásticas blancas; 6: domo de Morrón de Mateo; 7: sedimentos aluviales actuales.

Consequently, among the main processes expected in the bentonite engineered barrier, the alteration and/or transformation of Al-smectites are the most relevant, as a result of the interaction among smectite, temperature and geochemical conditions.

Based on these analogies, the neoformation of Fe (Mg)-rich smectites observed in the proximal zones of the natural system would be expected in the bentonite barrier of the repository, in which an enhanced Fe concentration close to the container can be induced as a result of its partial oxidation under intermediate redox conditions. In this scenario, no variations in the physicochemical properties, i.e. total exchange cations and BET specific surface area, of the bentonite barrier will occur, as this study demonstrated. However, under a stronger or longer interaction, the neoformation of trioctahedral smectites such as saponite-stevensite, Fe(II)-rich saponite or dioctahedral nontronite (as a function of the Mg and Fe(II)/Fe(III) activities in the environment, respectively), corrensite and Fe-Mg-rich chlorite may occur as recorded in some active geothermal and diagenetic systems (Yamada and Nakasawa, 1993; Beaufort *et al.,* 1995, 2001; Bril *et al.,* 1996; Robinson and Santana de Zamora, 1999; Mayayo *et al.,* 2000; Hover and Ashley, 2003). Under these circumstances, significant variations in the physicochemical and physicomecanical properties of the bentonite engineered barrier of a HLW deep geological repository could be expected.

Though the studies performed on the bentonites from the Cala de Tomate deposit were primarily focussed on the thermal effect (Fig. 21), the results do not allowed the establishment of any analogy in relation to this expected effect. Thus, the geology of the site showed that the contact between the Cala de Tomate volcanic dome and the bentonitised tuff is re-taken by faults, and that the bentonitisation process was mainly favoured by this faulting event.

The mineralogy of bentonites indicates that the major mineral is an Al-rich dioctahedral smectite (montmorillonite type), as in other bentonite deposits in the region (Reyes, 1977; Reyes *et al.,* 1987; Linares *et al.,* 1993; Delgado, 1993), including the Cortijo de Archidona deposit, from which the Spanish reference bentonite comes. The most significant and differential feature of the smectites from the Cala de Tomate deposit is the nature of their exchangeable cations, since Mg-Ca and Na-Mg-smectites coexist: Na-Mg-smectites are present in samples located in the deepest parts of the exploration exposures, whereas Mg-Ca-rich smectites are present in their upper parts with respect to the topographic surface.

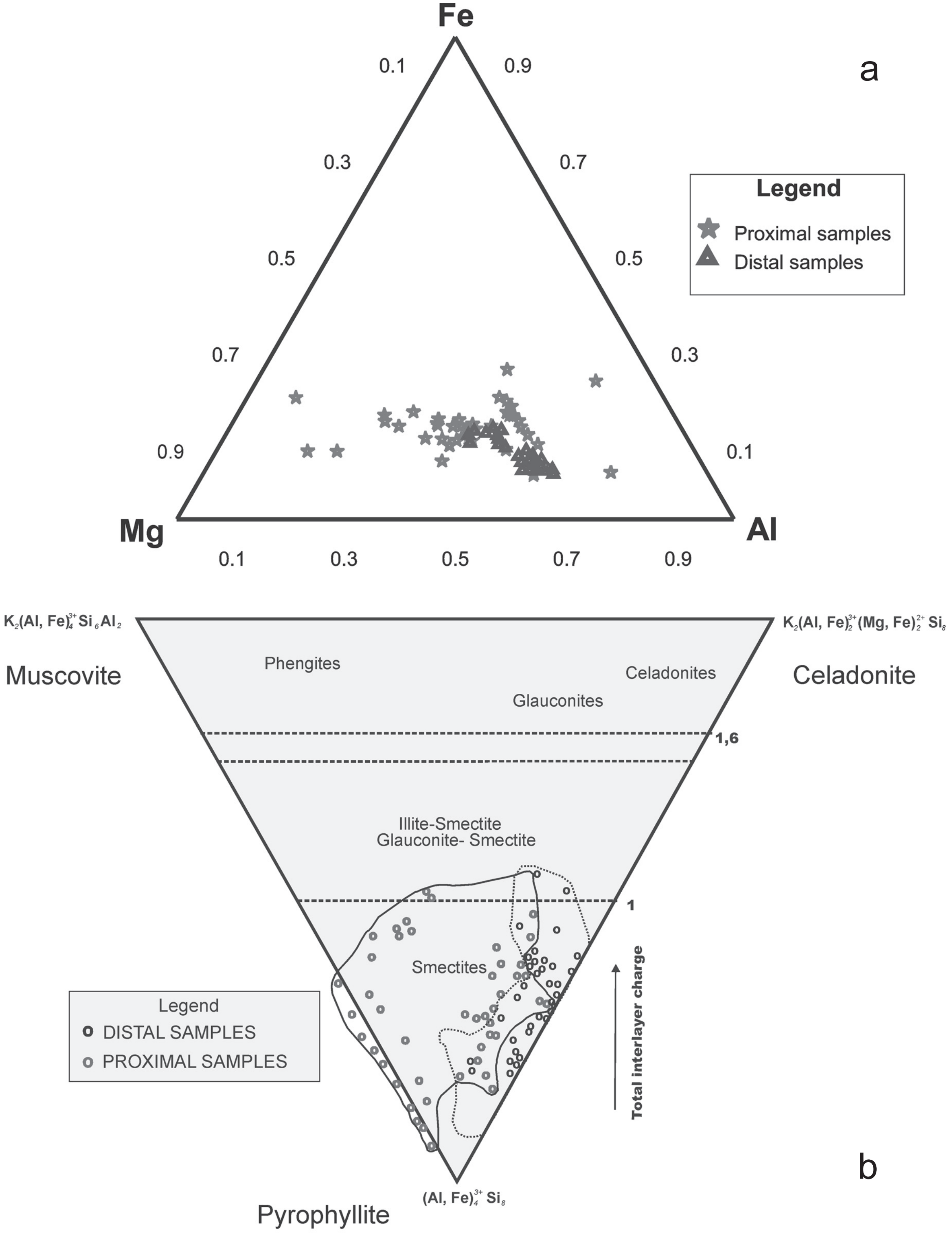

Fig. 20.- Morrón de Mateo. a) Fe-Mg-Al ternary diagram showing the octahedral cations of the smectites. Note the two evolutionary trends defined by the distal (Al-rich members) and proximal smectites (Mg- and Fe-rich end-members). b) Pyrophyllite-celadonite-muscovite ternary diagram on which smectites are represented according to the octahedral, tetrahedral and interlayer charges. Note that all the samples plot in the smectite domain and that the proximal smectite area overlaps the distal smectite one (Pérez del Villar *et al.,* 2005a).

Fig. 20.- Morrón de Mateo. a) Cationes octaédricos de las esmectitas en un diagrama ternario Fe-Mg-Al. Nótese las dos tendencies evolutivas definidas por las esmectitas distales (miembros alumínicos) y proximales (miembros finales magnésicos y férricos). b) Representación de las cargas octaédricas, tetraédricas e interlaminadas de las esmectitas en un diagrama ternario Pirofilita-celadonita-muscovita. Nótese que todas las muestras quedan en el dominio de las esmectitas y que el área proximal se solapa con la distal (Pérez del Villar *et al.,* 2005a).

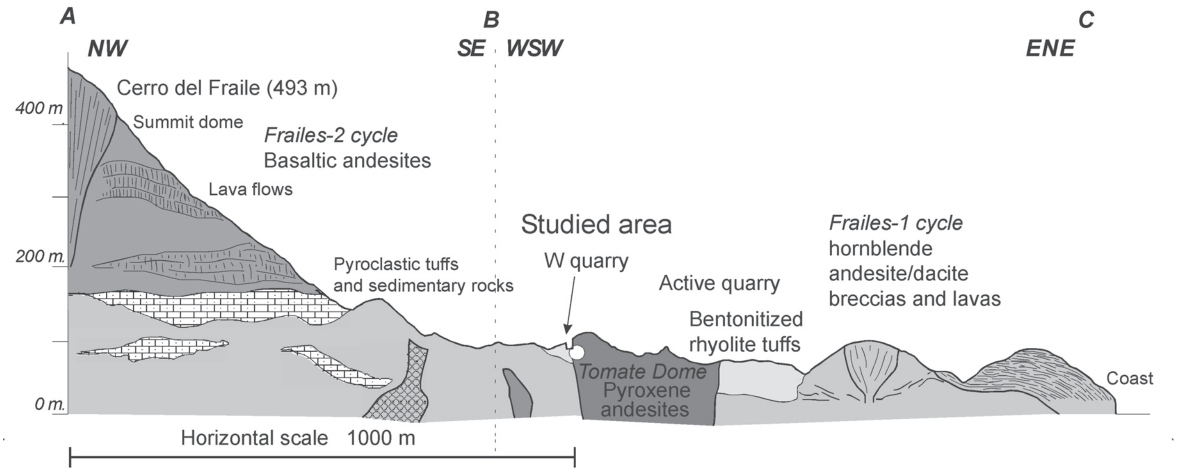

Fig. 21.- Geological cross section of the SE Frailes building, including the Cala de Tomate bentonite outcrops (Fernández-Soler, 1992). The figure shows the intrusive relationship between the Tomate dome and the partially-bentonitised rhyolitic tuffs.

Fig. 21.- Corte geológico de la sección SE del edificio Los Frailes, incluyendo los afloramientos de bentonita de Cala de Tomate (Fernández-Soler, 1992). La figura muestra la relación intrusiva entre el domo Tomate y las tobas riolíticas parcialmente bentonitizadas.

The isotopic signature of these smectites agrees with those formed in equilibrium with meteoric waters at <25ºC, whereas the isotopic signature of minor carbonates in some bulk samples suggests that these smectites were under submarine condition after their formation. As a consequence, it can be stated that these smectites were formed under meteoric diagenesis, particularly in the faulting zones originated after intrusion of the Cala de Tomate dome. However, the environmental conditions under which these smectites were primarily formed seem to be incompatible with the presence of Na, which is the main exchangeable cation in some specimens. This fact can be explained considering that the deposit was under submarine conditions after its formation. The high concentrations of Na^+ and Cl^- determined in soluble salts of the bulk samples seem to corroborate this hypothesis.

After emersion, the interaction between Na-Mg-smectites and fresh water produced cation exchange processes in the upper parts of the deposit. Thus, Na-Mg-smectites became Mg-Ca-smectites in the surface, whereas Na-Mg-rich smectites prevailed in the deeper parts of the bentonitised faulting zones.

The transformation of Ca-rich smectites into Na-rich smectites can also be expected in the bentonite barrier of a deep geological repository in the case that a Ca-rich bentonite is used and it is invaded by Na-rich saline water. Under these hypothetical conditions, Ca-rich bentonite becomes Na-rich and some of the most important features of the bentonite-engineered barrier, such as the reological and colloidal properties could be modified. Deep Na-rich saline waters and brines, regardless their origin, are frequent in crystalline basements suitable for radwaste disposals, such as the Canadian and Fennoscandinavian shields and the crystalline basement of Central and Western Europe, particularly in the Bohemian Massif and the Vienne district in W-France (Kloppmann *et al.,* 2002).

The Cortijo de Archidona deposit was selected as a natural analogue of the behaviour of bentonite influenced by natural saline waters, since it has been affected by different water intrusions during its recent geological history. The chemistry of the pore water can lead to important changes in the bentonite properties due to different processes such as illitisation, cementation, dissolution-precipitation of accessory minerals and cation exchange.

The Cortijo de Archidona deposit is related to two large fractures (NE-SW and N-E), which affect the volcano-sedimentary sequence (Fig. 22). This bentonite originated from the alteration of dark-coloured vesicular rhyodacitic glasses and light-coloured ignimbrites. The alteration process was favoured by the intense brecciation of these materials in the fracture zones, which in turn also allowed the passage of the alteration solutions. The bentonite mineralogy and microfabric, the pore water composition and the physico-chemical properties of different core samples taken from six 20-m depth boreholes were determined. Special emphasis has been given to the role of the water-bentonite interaction processes involving accessory non-clay minerals, which affect the bentonite cementation and its buffer capacity for pH and redox potential of the near-field pore waters.

Three zones can be distinguished in the bentonite deposit: i) the smectitic zone; ii) the contact zone with the

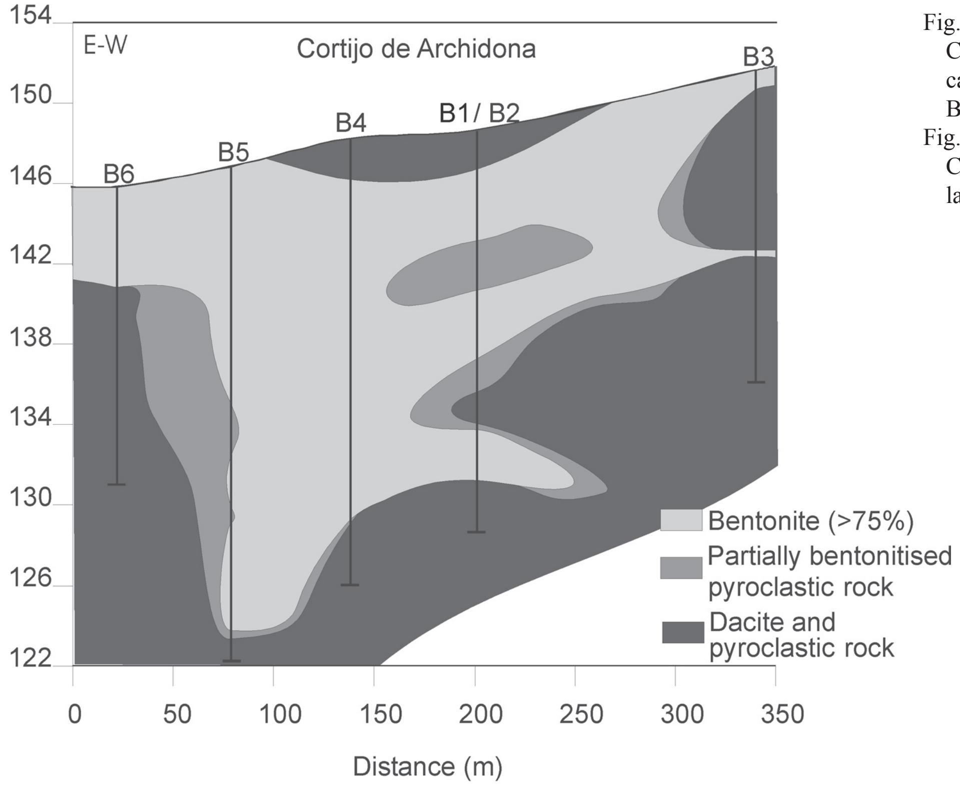

Fig. 22.- Geological cross-section of the Cortijo de Archidona deposit with indication of the location of boreholes B1 to B6.

Fig. 22.- Corte geológico del yacimiento Cortijo de Archidona con indicación de la posición de los sondeos B1 a B6.

volcanic rocks; and iii) the transitional zone between both of them. The smectitic zone is located at the central part of the deposit, where the major mineral phase (78-97 mass percent) is a dioctahedral Al-Fe rich smectite. The contact zone with the volcanic rocks is characterised by the presence of bentonite with important amounts of pyroclastic materials (>50 mass percent) and other clay minerals, apart from smectite, such as illite, chlorite and fibrous minerals of sepiolite-palygorskite type. The transitional zone between the bentonite massive zone and the bentonite in contact with the volcanic rocks corresponds to a bentonite with a 30-50 mass percent of pyroclasts.

Some properties like the chemical stability, the long-term durability, the swelling capacity and the high exchange capacity of the smectite of the Cortijo de Archidona deposit have been preserved during its geological history. The bentonite in the smectitic zone is almost water saturated and the clay minerals are stable. However, two types of heterogeneities have been found: 1) the chemical composition of the pore waters; 2) the composition of the exchangeable sites. The chemical composition of the pore waters, obtained by squeezing, varies from Na-Mg-SO_4 to Na-Cl water type, being Na-Cl type in the smectitic zone. The pore water salinity is higher in the upper part of the deposit and decreases downwards (Fig. 23), indicating a possible diffusive transport of seawater through the bentonite. The ionic strength varies from 0.23 to 0.02 M and the pH is neutral (6.8-8.0), which implies the stability of the clay minerals. According to the chemical composition of the pore waters and the stable isotopes study, two bentonite post-formational processes have been found. First, a seawater intrusion, since the Cl/Br and SO_4/Cl ratios are similar to those of seawater. Subsequently, an infiltration of new Ca-Mg rich meteoric waters. These waters interacted with the bentonite and modified the pore water chemistry and the concentration of cations in the exchangeable sites. The composition of the exchange complex is Ca-Mg type, with high contents of sodium. At the top of the deposit, where the salinity is higher, the content of sodium as exchangeable cation increases, replacing calcium. In any case, the bentonite has preserved a high concentration of solutes and its mineral stability. These Ca-Mg-rich meteoric waters caused the aforementioned new post-formational alteration of the pyroclastic rocks.

4. Summary and conclusions

The study of clays for their use as sealing materials in high-level radioactive waste repositories started in Spain in the late 80's. Smectites and illites were proposed at the beginning, as well as mixtures of them with quartz sand or crushed granite. Among the smectites, montmorillonites from the Cabo de Gata region (Almería) and

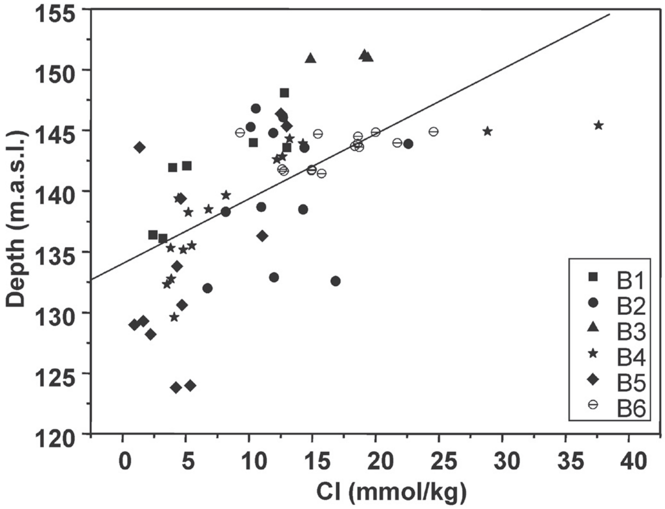

Fig. 23.- Chloride concentration as a function of depth in the pore waters squeezed from bentonite samples taken from different boreholes (B1 to B6) at the Cortijo de Archidona deposit.

Fig. 23.- Concentración de cloruros en función de la profundidad en las aguas intersticiales extraídas de muestras de bentonita tomadas de los sondeos B1 a B6 del yacimiento de Cortijo de Archidona.

saponites from the Madrid Basin (Toledo) were found to be suitable materials to construct clay barriers, since their mineralogical, geochemical, physicochemical, thermal, hydraulic and mechanical properties are the adequate ones. For its best compaction properties, a bentonite from the Cortijo de Archidona deposit (Almería) was selected as Spanish reference material. Detailed and specific studies were carried out in this clay, concerning particularly its alterability and its behaviour under conditions similar to those of a repository: temperature gradients, water flow and unsaturated conditions during the transient stage. As a continuation to the initial stages of the investigation, two new researching lines were opened: one of them devoted to the study of the bentonite under conditions as close as possible to those in the repository, at the laboratory and in large-scale tests; and the other to the study, by means of natural analogues, of the long-term evolution of the barrier. Due to the social and environmental repercussion of the radwaste disposal, the research on the areas presented is still ongoing.

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This paper is dedicated to Pedro Rivas, a pioneer in the study of some of the issues herein presented and the head of many of the research projects compiled. He has participated intensely in all the described investigations.

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