SELECTION AND CHARACTERIZATION OF A REFERENCE SEALING MATERIAL：THE SPANISH CASE

Villar María Victoria[1]，Astudillo Julio[2]，Huertas Fernando[2]

(1. *CIEMAT*，*Research Centre for Energy*，*Environment and Technology*，*Madrid* 28040，*Spain*；
2. *ENRESA*，*Empresa Nacional de Residuos Radiactivos S.A.*，*Madrid* 28043，*Spain*)

Abstract：The paper summarises the studies performed in Spain as regards the selection and characterization of clays suitable for sealing and backfilling of radioactive waste repositories. This research began in the 1980s under the auspices of ENRESA，the Spanish agency for nuclear waste management，and started by a survey of apt clay deposits and suppliers. The characterization 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 two bentonite deposits，whose detailed characterizations were carried out by several laboratories. These included the determination of thermo-hydro-mechanical properties，and of the impact of pre-heating，temperature and addition of quartz on these properties. The high expandability and low permeability of these materials led to the modification of the available experimental techniques and to the design of new equipment. 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，the behaviour of this bentonite under the conditions of a repository has been studied at laboratory and natural scale.

Key words：radioactive waste disposal；bentonite barrier；Spanish clays；montmorillonite；saponite

CLC number：TL 942^{+}.21 **Document code**：A **Article ID**：1000－6915(2006)04－0768－13

一种缓冲回填材料的筛选及其特性：西班牙实例

Villar María Victoria[1]，Astudillo Julio[2]，Huertas Fernando[2]

(1. CIEMAT，能源环境与技术研究中心，西班牙 马德里 28040；
2. ENRESA，国家放射性废物管理公司 S. A.，西班牙 马德里 28043)

摘要：介绍了西班牙在高放废物深地质处置中用于缓冲回填材料的泥岩的筛选及其特性的研究成果，这项研究在西班牙核废料管理委员会资助下进行，始于 20 世纪 80 年代，且在开始阶段主要是开展泥岩沉积层及黏土供应商

Received date：2005－08－30；**Revised date**：2005－12－20

Foundation item：Work co-funded by ENRESA，CIEMAT and the European Commission

Corresponding author：Villar María Victoria(1964－)，female，Ph. D.，graduated from at Universidad Complutense de Madrid，Madrid，Spain in 1987. She is presently the head of Soil Mechanics Laboratory at the Geological Disposal Division，CIEMAT(Madrid)，and her main research activities cover the expansive，unsaturated materials thermo-hydro-mechanical characterizations. E-mail：mv.villar@ciemat.es

的筛选工作。黏土这些特性与标准已被国际社会广泛接受，但进一步的研究主要涉及到泥岩的矿物纯度、持水特性、可塑性、低渗透性、较高的膨胀压力和热导性。经初步研究，确定两种膨润土沉积层被选中，并在实验室中对其特性进行了研究，主要包括：热－水－力特性的确定、预加热和温度的影响以及石英添加剂的作用。由于膨润土具有较高的膨胀性以及低渗透性，因而必须对传统的试验技术进行改进，并设计出新的试验设备。最终确定 Cortijo de Archidona(Almería)选为西班牙膨润土的供应区，其开采的膨润土已在近期结束的数个研究课题中得到了应用。无论是从矿物学、热学、水力学、力学和地质化学，还是从可变性等方面看来，该区膨润土的特性都是最好的；另外，处置库中膨润土的变化特征在实验室以及现场都已经作了相应的研究。

关键词：放射性废物处置；膨润土屏障；西班牙泥岩；蒙脱土；皂石

1　INTRODUCTION

The generally accepted option for the definitive disposal of high-level radioactive wastes(HLW) consists in their disposal in stable deep geological formations(500－1 000 m). The safety of this disposal concept is based on the existence of a series of superimposed natural and artificial barriers to guarantee isolation(multi-barrier concept)：natural barriers，constituted by the host rock，and artificial(or engineered)，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. 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，the use of sodium bentonite(rocks made up of clay minerals belonging to the smectites group，in which montmorillonite is the most common species) compacted in the form of high density blocks as sealing material is proposed[1]，since it provides the following characteristics：

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

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

(3) Sufficient thermal conductivity，to prevent the generation of excessive thermal gradients.

(4) Mechanical resistance to withstand the weight of the canister.

(5) Mechanical properties guaranteeing the homogeneity 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[2] are as follows：

(1) Good compressibility，ensuring ease in processing，handling and transport to the disposal facility.

(2) 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.

(3) Nonexcessive swelling pressure，to avoid damage to the system.

(4) 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.

(5) 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[3，4].

Since the end of the 1980s，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 to the aggregates，tests have been performed using crushed granite，crushed basalt，zeolites，quartz and graphite. The main objective of adding inert aggregates is to increase the thermal conductivity of the barrier，and to improve the mechanical resistance of the compacted blocks and reduce the cost of the material.

The Spanish concept for deep geological disposal of HLW(almacenamiento geológico profundo，AGP) was developed by ENRESA from 1990，with the basic objective of "avoiding 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 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 Fig.1 for the granite case.

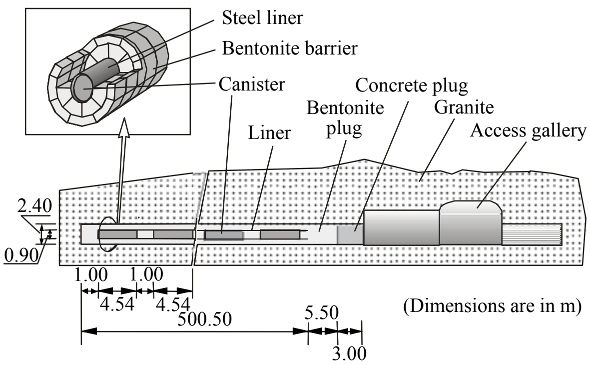

Fig.1　Longitudinal section of a disposal drift for the Spanish reference granite case[5]

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 as the backfilling material for the galleries and cavities. The dry density 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 ℃. 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 unpublished results of each phase of the research.

2　STUDY OF CLAY BARRIERS IN SPAIN：THE 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[5]. This study had three objectives：

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

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

(3) 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 from different locations. An initial semi-quantitative determination of the mineralogy allowed 50% of the samples to be excluded because of their content of phyllosilicates being lower than 65%. In accordance with the mineralogy of the fraction of less than 2 μm(Fig.2)，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)(samples 25，26 and 28 to 30).

Finally，two bentonites were selected that had not been subjected to treatment in the factory：a bentonite from the Cortijo de Archidona deposit，in Almería (sample 26)，and an illite from Zaragoza(sample 15)，these being chosen for their low carbonate and

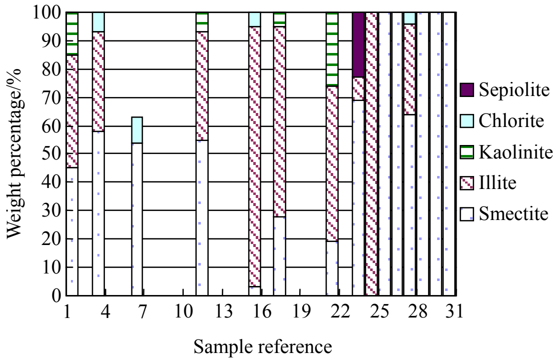

Fig.2　Mineralogical composition of the less than 2 μm fraction of the initially selected samples[6]

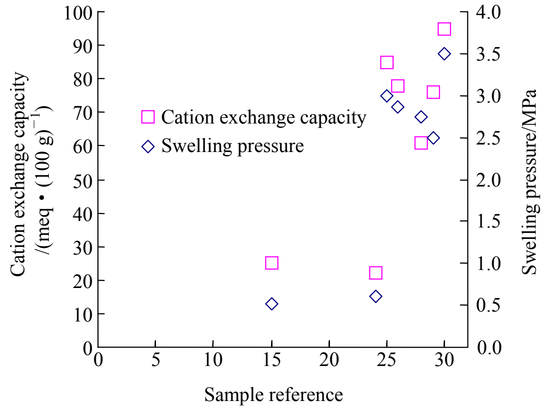

Fig.4　Cationic exchange capacity and swelling pressure of the initially selected samples(samples 15 and 24 are illites，the rest are smectites)[6]

colloidal mineral content and high degree of plasticity and compressibility(Fig.3).

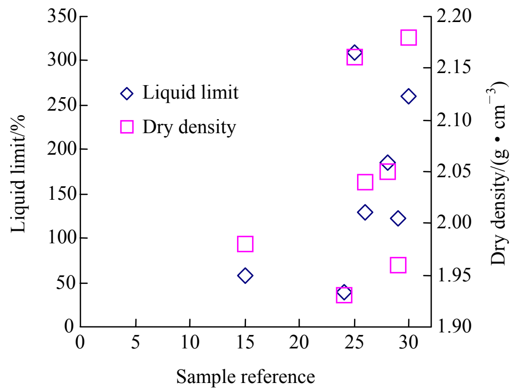

Fig.3　Plasticity(expressed as liquid limit) and compressibility (expressed as dry density after uniaxial compaction at 123 MPa of the clay with hygroscopic water content) of the initially selected samples(samples 15 and 24 are illites，the rest are smectites)[6]

Analysis of the mechanical，hydraulic，thermal and physicochemical properties of both，and their behaviour when mixed with crushed granite and when being heated，allowed the following conclusions[6] to be drawn：

(1) There are clays in Spain that might be used as backfilling and sealing materials.

(2) It is advisable to use smectitic clay and not illitic clay as backfilling and sealing material，due to its greater swelling pressure，specific surface and cation exchange capacity(Fig.4). 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.

(3) Crushed granite may be used as an additive to the smectite，as long as it does not exceed 25% of the mixture. Above this percentage，swelling pressure decreases and hydraulic conductivity increases(Fig.5) out of the acceptable ranges.

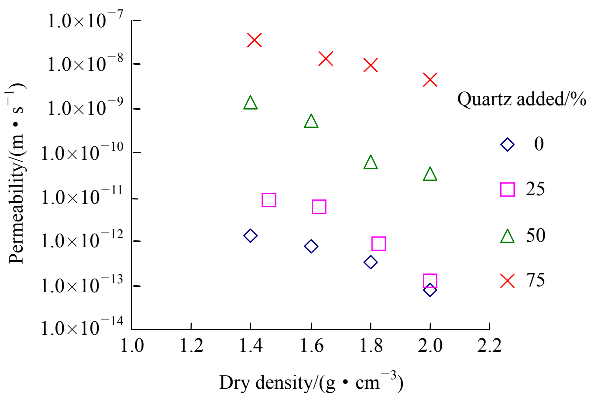

Fig.5　Hydraulic conductivity of montmorillonite(sample 26)/ quartz mixtures[6]

(4) The heating of the clays at temperatures above 100 ℃ negatively modify their properties，since plasticity，swelling capacity，strength and specific surface area are reduced.

2.2　Study on two smectite-bearing areas

Parallel to the above，two Spanish areas with important deposits of smectite clays that might be used as backfilling and sealing materials for a future HLW disposal facility were studied. These areas were the volcanic region of Cabo de Gata，in Almería，and the Tertiary Basin of Madrid in the province of Toledo.

A preliminary characterization of 30 bentonite outcrops(10 samples per outcrop) in the Cabo de Gata region allowed the selection of three deposits(Cortijo de Archidona，Morrón de Mateo and Los Trancos) for a comparative study. These deposits were selected on the basis of the following criteria：(1) the smectite content should be higher than 70%－75% and the minimum estimated reserves should be in the order of 106×10^3 kg. The bentonites from Cortijo de Archidona are very pure and have outstanding colloidal properties；(2) the Los Trancos deposit—also of a great purity—have the major bentonite reserves；and (3) the bentonites from Morrón de Mateo have important quantities of sand，what could avoid the addition of additives[7]. The average mineralogical composition of the bentonites from the selected deposits is shown in Table 1.

Table 1　Average mineralogical composition of the bentonites from the selected deposits in the Almería area[7]　　%

Mineral	Los Trancos	Cortijo de Archidona	Morrón de Mateo
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

On the other hand，the mineralogical and physicochemical properties of 28 samples taken from three clay quarries located in the Tertiary Basin of Madrid(Toledo area) were determined：the Cerro del Águila-Cerro del Monte deposit，the Santa Bárbara deposit and the Yuncos deposit[8]. Table 2 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 natures. In fact，they are composed of smectites of the saponite-stevensite group(Mg-smectites). Moreover，the clays from Cerro del Águila were of saponitic nature(Al-substituted tetrahedral-charged)，what is very rare in the sedimentary environment in which they formed.

In two samples from each deposit，it determined 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 by using compacted samples. The results obtained are to be found in relative studies[10－13]，and some of them are shown in Table 3.

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

Table 2　Properties of clays from the Toledo area and limit values of these properties established for sealing and backfilling purposes[9]

Name	Fraction size (<2 μm)/%	Smectite content/%	CEC /(meq • (100 g)$^{-1}$)	Organic matter /%	$CaCO_3$ /%	Amorphous content/%		Specific surface BET /(m^2 • g^{-1})	Swelling pressure* /MPa
						SiO_2	Fe_2O_3		
Limit value	>80	>60	>60	<0.2	<6.0	<1.00			
Cerro del Águila	93	82	77	0.07	－	0.20	－	155	6
Santa Bárbara	85	kerolite-stevensite	49	0.37	0.1	0.20	0.03	257	12
Yuncos	88	81	73	0.09	5.0	0.06	0.14	12	4

Notes：“*” is for dry density of 1.4 g/cm^3.

Table 3　Physical properties of samples from Almería and Toledo areas

Reference	Phyllosilicates /%	Liquid limit/%	Specific surface* /($m^2 \cdot g^{-1}$)	Hygroscopic Water content/%	Dry density** /($g \cdot cm^{-3}$)	Thermal conductivity/($W \cdot (m \cdot K)^{-1}$)	Remarks
MY-A	82	220	304	16.1	1.58	0.87	Yuncos
MY-B	84	133	212	13.1	1.79	1.07	
MCA-A	90	237	216	16.1	1.66	0.87	Cerro del Águila-Cerro del Monte
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	Santa Bárbara
MSB-B	94	137	150	17.0	1.64	0.99	
E－5	74	122	341	18.6	1.72	1.03	Morrón de Mateo
E－6	66	85	332	13.3	1.78	1.11	
T－3	95	97	198	20.6	1.64	1.15	Los Trancos
T－4	98	90	152	19.5	1.64	1.15	
S－1	96	139	553	19.0	1.73	1.24	Cortijo de Archidona
S－2	86	213	517	15.8	1.82	1.21	

Notes：(1)　“*” is Methylene blue method；(2)　“**” denotes　“after uniaxial compaction at 100 MPa with hygroscopic water content”.

into account in making the selection were those indicative of the suitability of the material for use as a 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 where the latter is an additional requirement for the manufacturing of high density blocks. This aspect can be checked in Fig.6 for the samples from Toledo and in Fig.7 for the samples from Almería[10]：for a given compaction energy(modified proctor)，the densities reached by the samples of Cerro del Águila(“MCA” in Fig.6) and Cortijo de Archidona(“S” in Fig.7) are the highest.

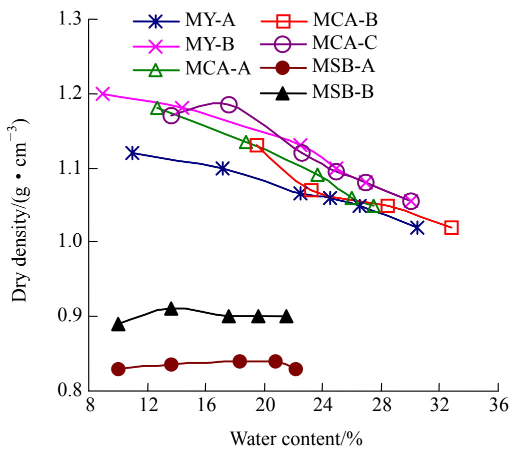

Fig.6　Results of compaction tests(modified proctor) on samples from Toledo area[10]

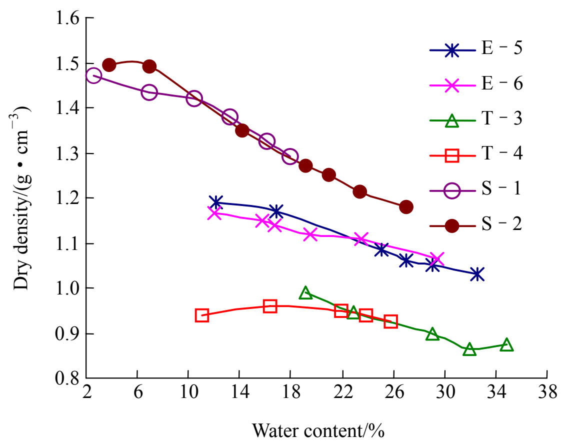

Fig.7　Results of compaction tests(modified proctor) on samples from Almería area[10]

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 characterization of their physicochemical properties and alterability was detailed. For this purpose，a sample of 5 000 kg from each deposit was used，dried at 60 ℃ to water content of close to 10% 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 ℃，50%－60% percent relative humidity).

The characterization included the tests for 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 clay to different temperatures. The following studies were carried out on both clays：

(1) 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.

(2) Unconfined compressive strength：influences of sample dry density and water content，of the granulometry used and of the addition of different proportions of quartz sand added.

(3) Free swelling.

(4) Swelling pressure：analysis of the influence of dry density and of the proportion of quartz sand added.

(5) Saturated hydraulic conductivity for different dry densities，proportions of quartz sand added and measurement temperature.

(6) Thermal conductivity：analysis of the influence of dry density，water content and the proportion of quartz sand added.

(7) Oedometric tests.

(8) Triaxial tests.

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

(10) Determination of adsorption-desorption isotherms.

(11) 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 ℃，respectively(Fig.8). Also determined were the modifications caused by heating as regards mineralogy，

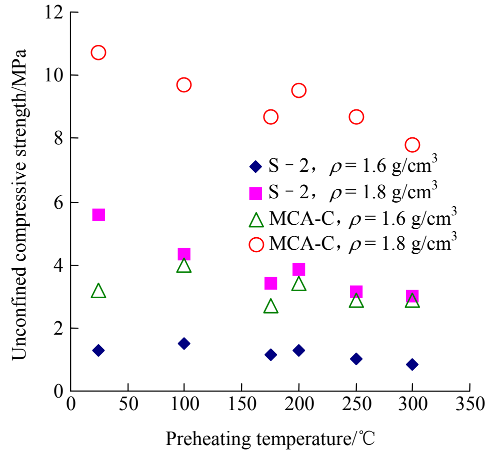

Fig.8　Unconfined compressive strength of specimens obtained by uniaxial compression of preheated bentonite with 10 percent water content[10]

specific gravity，specific external surface and microstructure observed through electron microscopy.

In addition，hydrothermal alteration experiments were conducted with the objective of testing the stability of each type of clay under heating up to 175 ℃ in an aqueous solution environment dominated by KCl salts(0.01－0.50 mol/L). 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[13，14]. The saponite from the Madrid Basin was stable up to 175 ℃，showing no sign of illitization or crystallochemical changes[15，16].

These studies complemented the results obtained at CIEMAT[9，10，17]，and allowed the montmorillonite from the Cortijo de Archidona deposit，reference S－2，to be definitively selected，mostly for its better compaction properties，although the both clays (montmorillonites and saponites) in fact fulfilled the requirements for use as a barrier material. Good compressibility was taken as selection criterion because it is a key property for the manufacture of blocks，which is an essential aspect of the installation of the barrier. The conclusions drawn during this phase were as follows：

(1) Both uniaxial and dynamic compressions were adequate for the production of high density compacted blocks.

(2) The grain size distribution did not modify the final density of the blocks.

(3) Saturated hydraulic conductivity and swelling pressure depend on the dry density of the clay in accordance with an exponential relation(Fig.9). A dry density of 1.60 g/cm^3 satisfies the hydraulic requirements of the barrier.

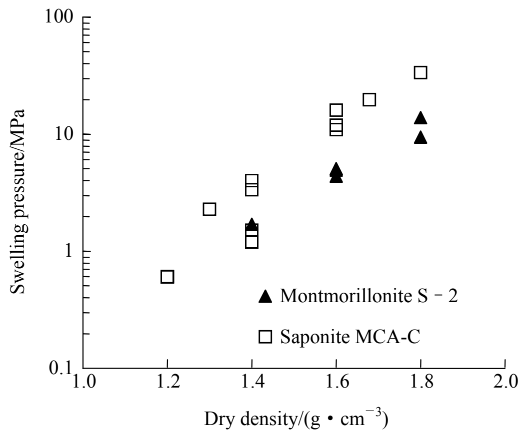

Fig.9　Swelling pressure of compacted specimens of the two selected bentonites

(4) 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.

(5) The thermal conductivity of the material increases with dry density and water content.

(6) 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，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[18]. Fig.10 shows how the thermal conductivity of blocks of a given dry density does not increase with the addition of quartz.

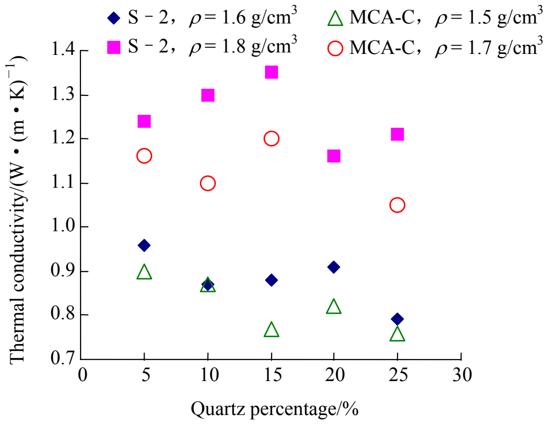

Fig.10　Thermal conductivity of bentonite/quartz mixtures for samples S－2 and MCA-C[10]

Simultaneously，industrial type uniaxial compaction tests were performed on both clays[19，20]. Also carried out was a clay barrier validation test in a vertical shaft，performed at the Fanay-Silord mine(France) by using the S－2 clay[21]. The vertical disposal was one of the concepts considered at that moment.

2.4 Thermo-hydro-mechanical and geochemical characterization of the reference clay(1991－1995)

Once selected，the second phase of characterization of the S－2 clay from the Cortijo de Archidona deposit began in 1991. For these studies，24×10^3 kg of bentonite were used，prepared at the factory by drying at 60 ℃ 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 characterization 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[22].

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. Fig.11 shows the main components of a thermo-hydraulic test, with the cell in the central part.

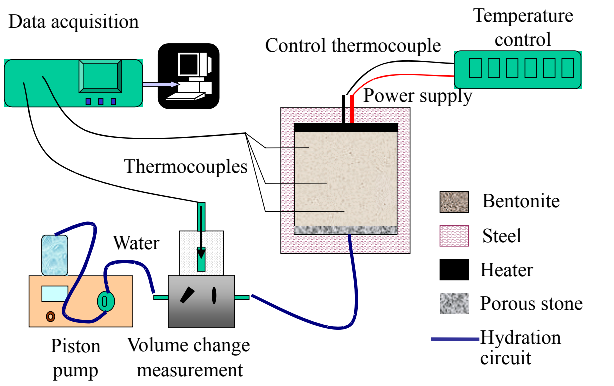

Fig.11　Schematic diagram of assembly for the performance of laboratory thermo-hydraulic test

This research provided information about the temperature field inside the clay, the variables affecting water intake, the water content and dry density distribution, the chemical and physical changes occurred, the generation and evolution of saline fronts and the variation of hydro-mechanical properties of the bentonite. Some of the conclusions of this work[23, 24] are as follows:

(1) The temperatures recorded within the clay subjected to heating and hydration in thermo-hydraulic cells depend on the geometry and power of the heater and, for the same boundary conditions, depend also on the water content of the clay, since any increase in water content leads to an increase in thermal conductivity.

(2) The speed of water intake for a constant injection pressure and clay density depends at each moment on the water content of the clay, in other words on suction, and no contribution by the thermal gradient has been identified in the process, even though this does not exist(Fig.12).

(3) The water content of the clay increases as the

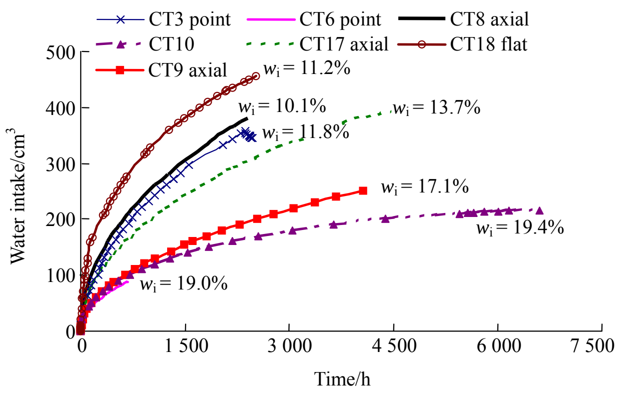

Fig.12　Velocity of hydration in the different thermo-hydraulic tests in cells, with indication of initial water content (w_i) and of type of heater(point, axial, flat)[24]

hydration front progresses, and the dry density decreases due to swelling. This implies an increase in density in the areas furthest from the hydration surface, as a result of the compression exercised by the expanding clay, since the entire process occurs at a constant volume. When the clay is heated by the opposing front, the distribution of water contents is initially affected by the thermal gradient, due to the desiccation that takes place close to the heater, but as saturation is approached, the profile of water contents and of densities becomes homogeneous. On heating, the increase in density of areas located at a distance from the hydration front is accentuated, since there is shrinkage by the loss of water content caused by the temperature.

(4) As hydration progresses and saturation is reached, sealing of the bentonite blocks occurs, even when these are being heated.

(5) Three mechanisms involved in the transport of solutes, and acting jointly, have been identified:

(i) Advection: with the hydration water, that causes the dissolution of salts that are entrained in ionic form towards more distant areas. This mechanism is particularly intense in the case of chlorides, which are rapidly dissolved and transported. Transport by advection operates regardless of the existence or not of a thermal gradient, although if one does exist the phenomenon is accentuated.

(ii) Advection-convection: in those tests in which there has been heating, and regardless of whether or not there has been hydration，a concentration of salts may be observed in the areas surrounding the heater，this being attributed to a process of advection-convection. The spatial extent of this mechanism is particularly limited，and it would appear to affect sulphates with greater intensity.

(iii) Diffusion：this is a slow process that is not perceived until such time as a high degree of saturation has been reached and an important gradient of concentrations has been established by other mechanisms. It is difficult to identify because it is masked by other phenomena，and requires long experimentation periods. This process gives rise to a homogenization of the concentration of soluble salts in the clay overall，since it acts contrary to the other two mechanisms described above.

(6) The saline fronts created cause the corrosion of the metallic elements of the system，leading to the formation of iron oxides and copper salts.

(7) The exchange complex is affected by the establishment of a thermal gradient. Particularly clear is the decrease in sodium and potassium towards the hotter areas，following the profile of the isotherms，this occurring even in the absence of hydration. Exchangeable magnesium also undergoes redistribution，conditioned by the thermal gradient，its content increasing towards the hotter areas.

(8) No important and/or preferential concentrations of free silica were observed in any of the experiments，as a result of which it is assumed that no silica cementations have occurred.

(9) The swelling pressure and hydraulic conductivity of samples subjected to heating and hydration are related to their dry density and water contents，and stay in values similar to those of the untreated clay.

Furthermore，study of the material in the unsaturated state was focused on determination of the suction/water content relation of the clay with different values of initial water content and density，and on the performance of oedometric tests with controlled suction. The oedometric tests followed two types of paths：(1) drying/wetting under constant load，followed by loading/unloading at the last value of suction reached；and (2) wetting/drying under constant vertical load，followed by loading/unloading at the last value of suction reached. The maximum vertical pressure applied during these tests was 5 MPa，and the maximum suction 140 MPa. This implies that the water content of the clay in these tests was never below the hygroscopic water content. 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[25，26].

Likewise，the characterization 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[24，27].

3　STUDIES OF THE BENTONITE AS ENGINEERED BARRIER IN REAL CONDITIONS

In the research and development(R&D) plans performed prior to 1994，which have been partially summarised above，ENRESA studied sources of supplement of the materials to be used in the clay barrier along with its thermal，hydraulic，mechanical and geochemical behaviour. Likewise，integral characterization studies were performed on granitic massifs. The next step in gaining insight into the feasibility of the AGP concept，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[28]. 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[29]. 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：(1) an in-situ test under natural conditions and at full scale；(2) a test on an almost full-scale mock-up；and (3) 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[28].

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 was 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).

The laboratory tests included characterization tests and tests for the acquisition of parameters，as well as THM and THG tests，and 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[28，30－34]. 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；and (3) the effect of temperature and salinity on the hydro-mechanical properties. 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；and (3) the processes of sorption and transport of radionuclides in the bentonite. Besides，the variation of the hydro-mechanical and geochemical properties of the bentonite subjected to five years of operation under repository conditions(in-situ test) were analysed[35].

The clay used for all the Project experiments，both the large-scale and the laboratory tests—the FEBEX clay，comes from the Cortijo de Archidona deposit(Almería)，the same from which the S－2 bentonite was taken 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 modifications 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 has been very useful[30].

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 1980s. 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 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 on 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. The initial stages of the investigation were followed by the study of the bentonite under conditions as close as possible to those in the repository，both at the laboratory and in large-scale tests.

References(参考文献)：

[1] Pusch R. Highly compacted sodium bentonite for isolating rock-deposited radioactive waste products[J]. Nuclear Technology，1979，45：153－157.

[2] Yong R N，Boonsinsuk P，Wong G. Formulation of backfill material for a nuclear fuel waste disposal vault[J]. Can. Geotech. J.，1986，23(2)：216－228.

[3] Pusch R，Gray M N. Sealing of radioactive waste repositories in crystalline rock[A]. In：OECD-NEA/CEC Workshop "Sealing of Radioactive Waste Repositories"[C]. Braunschweig：[s. n.]，1989. 1－14.

[4] Güven N. Longevity of bentonite as buffer material in a nuclear-waste repository[J]. Eng. Geol.，1990，28(3/4)：233－248.

[5] ENRESA. FEBEX，Pre-operational Stage Summary Report[M]. Madrid：Publicación Técnica ENRESA，1997.

[6] Mingarro E，Rivas P，Villar M V，et al. Characterization of clay(bentonite)/crushed granite mixtures to build barriers against the migration of radionuclides：diffusion studies and physical properties. Task 3—characterization of radioactive waste forms(A series of final reports(1985－1989)，No.35，Nuclear Science and Technology Series)[R]. Luxembourg：Commission of the European Communities，1991.

[7] Linares J，Huertas F，Reyes R B，et al. Caracterización de Bentonitas Como Materiales de Sellado en Almacenamientos de Residuos Radiactivos[M]. Madrid：Publicación Técnica ENRESA，1993.

[8] Cuevas J. Caracterización de Esmectitas Magnésicas de la Cuenca de Madrid Como Materiales de Sellado. Ensayos de Alteración Hidrotermal[M]. Madrid：Publicación Técnica ENRESA，1992.

[9] Rivas P，Villar M V，Campos R，et al. Caracterización de materiales de relleno y sellado para almacenamiento de residuos radiactivos：bentonitas españolas[R]. Madrid：CIEMAT-DT-TG Report，1991.

[10] Villar M V，Dardaine M. Contribución a la selección de una arcilla española como material de relleno de un almacenamiento de combustible irradiado en roca dura. Resultados de la Fase I. Contrato cea/enresa A2845(Rapport Technique DRDS nº 244 Marzo)[R]. Fontenay-aux-Roses：CEA，1990.

[11] Villar P D L. Caracterización mineralógica y geoquímica de algunas muestras de bentonita procedentes de la Cuenca terciaria de Madrid(Yuncos，Toledo)[R]. Madrid：CIEMAT Report，1989.

[12] Villar P D L. Caracterización mineralógica y geoquímica de algunas muestras de bentonita procedentes de la provincia de Almería[R]. Madrid：CIEMAT Report，1989.

[13] Cuevas J，Pelayo M，Rivas P，et al. Characterization of Mg-clays from the Neogene of the Madrid Basin and their potential as backfilling and sealing material in high level radioactive waste disposal[J]. Applied Clay Science，1993，(7)：383－406.

[14] Linares J，Huertas F，Barahona E. Conversion time from smectite to illite：a preliminary study[J]. Applied Clay Science，1992，(7)：125－130.

[15] Cuevas J，Medina J A，Leguey S. Saponitic clays from Madrid Basin：accessory minerals influence in hydrothermal reactivity[J]. Applied Clay Science，1992，(7)：185－199.

[16] Cuevas J，Leguey S，Pusch R. Hydrothermal stability of saponitic clays from the Madrid Basin[J]. Applied Clay Science，1994，(8)：467－484.

[17] Villar P D L，Cruz B De La，Cózar J S. Estudio mineralógico，geoquímico de alterabilidad de las arcillas de Serrata de Níjar(Almería) del Cerro del Monte(Toledo)[R]. Madrid：CIEMAT Report，1991.

[18] Villar M V，Rivas P. Hydraulic properties of montmorillonite-quartz and saponite-quartz clay mixtures[J]. Applied Clay Science，1994，(9)：1－9.

[19] Martín P L，Dardaine M. Resultados preliminares de compactación uniaxial industrial sobre dos bentonitas españolas seleccionadas：mac-c de la Cuenca de Madrid S－2 de la zona de Almería. Resultados de la Fase I. Contrato CEA/ENRESA A2845[R]. Fontenay-aux-Roses：Rapport Technique RDD，1990.

[20] Martín P L，Dardaine M，Lajudie A. Resultados de compactación uniaxial industrial sobre una bentonita española seleccionada：S－2 de la zona de Almería. Resultados de la Fase I. Contrato cea/enresa A2845[R]. Fontenay-aux-Roses：Rapport Technique DSD，1990.

[21] Astudillo J，Olmo Del C，Rivas P，et al. Field test for the demonstration of the emplacement feasibility of clay buffer material as engineered barrier in crystalline formation(Volume 3). development of the industrial manufacturing processes and field validation of the buffer material concept[R]. Luxembourg：EUR European Commission.

1993.

[22] Villar M V. Thermo-hydro-mechanical Characterization of the Spanish Reference Clay Material for Engineered Barrier for Granite and Clay HLW Repository：Laboratory and Small Mock-up Testing[M]. Madrid：Publicación Técnica ENRESA，1995.

[23] Villar M V，Cuevas J，Martín P L. Effects of heat/water flow interaction on compacted bentonite：preliminary results[J]. Eng. Geol.，1996，41(2)：257－267.

[24] Villar M V，Fernández A M，Cuevas J. Caracterización geoquímica de bentonita compactada：efectos producidos por flujo termohidraúlico. (Versión 1，technical report CIEMAT/IMA/54A15/6/97)[R]. Madrid：FEBEX report 70－IMA-M－0－2，1997.

[25] Villar M V. First results of suction controlled oedometer tests in highly expansive montmorillonite[A]. In： Alonso E E， Delage P ed. Unsaturated Soils. Proc. the 1st Int. Conf. Unsaturated Soils(Paris)[C]. Rotterdam：A. A. Balkema，1995. 207－213.

[26] Villar M V，Martín P L. Suction controlled oedometer tests in montmorillonite clay. preliminary results[A]. In： Bentley S P ed. Engineering Geology of Waste Disposal. Geological Society Engineering Geology Special Publication No. 11[C]. London：The Geological Society，1996. 309－311.

[27] Cuevas J，Villar M V，Fernández A M，et al. Pore waters extracted from compacted bentonite subjeted to simultaneous heating and hydration[J]. Applied Geochemistry，1997，12：473－481.

[28] ENRESA. FEBEX Project，full-scale engineered barriers experiment for a deep geological repository for high level radioactive waste in crystalline host rock(Final Report)[R]. Madrid：Publicación Técnica ENRESA，2000.

[29] ENRESA. Almacenamiento geológico profundo de residuos radiactivos de alta actividad(AGP)，diseños conceptuales genéricos[R]. Madrid：Publicación Técnica ENRESA，1995.

[30] ENRESA. FEBEX Bentonite：origin，properties and fabrication of blocks[R]. Madrid：Publicación Técnica ENRESA，1998.

[31] Villar M V. Thermo-hydro-mechanical characterization of a bentonite from Cabo de Gata，a study applied to the use of bentonite as sealing material in high level radioactive waste repositories[R]. Madrid：Publicación Técnica ENRESA，2002.

[32] Fernández A M. Caracterización y modelización del agua intersticial de materiales arcillosos：estudio de la bentonita de Cortijo de Archidona[Ph. D. Thesis][D]. Madrid：University Autónoma de Madrid，2003.

[33] Missana T，Fernández A M，García-Gutiérrez M，et al. FEBEX II Project. THG Laboratory Experiments[M]. Madrid：Publicación Técnica ENRESA，2004.

[34] Lloret A，Romero E，Villar M V. FEBEX II Project，final report on thermo-hydro-mechanical laboratory tests[R]. Madrid：Publicación Técnica ENRESA，2004.

[35] Villar M V，Fernández A M，Rivas P，et al. Task 141：Postmortem bentonite analysis. EC Contract FIKW-CT-2000-00016，Deliverable D11[R]. Madrid：FEBEX Technical Report(70－IMA－M－6－7 v0. CIEMAT)，2004.