INFLUENCE OF PHYSICO-CHEMICAL, CRYSTALLOCHEMICAL AND COMPOSITIONAL PROPERTIES OF CLAY MINERALS ON EROSION PROCESSES

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INTRODUCTION

An understanding of the main mechanisms of colloid and gel layer formation from compacted bentonite during bentonite erosion is one of the main objectives of the BELBAR Project. The erosion mechanisms and colloid generation process are influenced by the physico-chemical, crystallochemical and compositional properties of the clay minerals, which are analysed in this work. The settling and flocculation processes of the clay particles depends on a lot of factors, such as the size and shape of the particles, surface properties, ionic strength of the incoming water, etc. For example, smectite particles in gels and suspensions are strongly influenced by: a) decreases in dry densities of the compacted bentonite due to swelling or changes in the chemical stability of smectite (montmorillonite/bentonite volume fraction or concentration), b) pore water/groundwater chemistry: ionic strength (I), pH, chemical composition, which govern the edge charge; c) changes in cation composition at the interlayer sites (in particular the Ca/Na content), and d) crystallochemistry of the clay minerals.

Different tests about the formation and stability of colloids from compacted bentonite have shown that degree of erosion is related to the quantity of smectite in the system and, therefore, the presence of other minerals and/or different clay minerals seems to affect the erosion of bentonite (Missana et al., 2015; Alonso et al., 2015). Indeed, bentonite is defined as a naturally occurring material that is composed predominantly of the swelling clay mineral montmorillonite (>75%). However, it contains more than one type of minerals (main and accessory minerals), and other type of clay minerals can be present. Furthermore, chemical and structural heterogeneity is typical for smectites.

Therefore, a study of the properties and compositional characteristics of different bentonites and clay minerals has been performed in other to identify which ones play a major role on the colloid generation process and, hence, in the bentonite erosion behavior.

EXPERIMENTAL MATERIALS

Around 40 years ago few commercial high quality bentonites were acquired for the study of bentonites as buffer and backfill materials in the construction of engineering barrier systems (EBS) for the isolation of high-level radioactive waste. The natural selected bentonites are industrially processed to fabricate highly compacted bentonite blocks, which have been used in different *in situ* large-scale EBS experiments (e.g., FEBEX-*in situ*, LOT, Prototype, TBT, etc.) and Mock-Up tests. Nowadays, new reference designs for the EBS consists on compacted blocks and pellets for filling the gap between the bentonite compacted blocks and the host-rock (e.g., EB-Experiment and FE experiments at Mont Terri, Switzerland).

In this work, different raw bentonites and clay materials were analysed, which have different structural characteristics: 2:1 (TOT) or 1:1 (TO) layer type, Di- or Tri-octahedral sites, TOT layers with low or high layer charge, charge location at tetrahedral or octahedral sites, dioctahedral clay minerals with cis- or trans-vacant positions. These clay minerals can be can be grouped as: a) Ca-Mg smectites (RO2K6-F02, FEBEX, Ibeco, Saz-2) or Na-smetites (MX-80, Nanocor, MSU, Sabenil S65, B75), b) bentonites made up of low layer charge smectites: beidellite SBdI-1, Ypresian Clays from Belgium (YD40, YK38); c) bentonites made up of high layer charge smectites; d) other type of clay minerals: saponite (MCA-C, B64), nontronite (NAu-1), illite (illite du Pui, IdP-2), kaolinite (KGa-1b); and e) granular bentonite material (Pellets) used at Mont Terri Research Laboratory: GBM non activated Na-smectite (FE-Experiment) and GBM non activated Ca-Mg smectite (EB-Experiment).

MX-80 (Wyoming deposit, USA) FEBEX (CA deposit, Spain) Sabenil S65 (Rockle deposit, Czech R.)

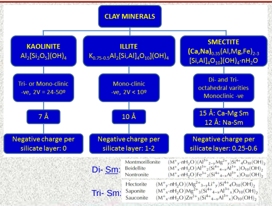
GBM non activated Na-Sm (FE Experiment)

GBM non activated Ca-Mg-Sm (EB Experiment)

Ypresian Clays (Kallo 38, Belgium)

EXPERIMENTAL RESULTS

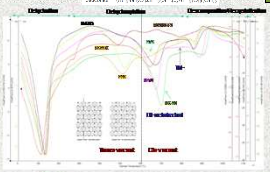
MINERALOGICAL ANALYSIS

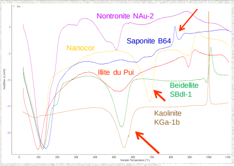


Mineralogy by XRD

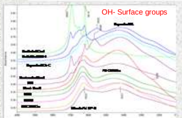
	FEBEX	Ibeco	R0-F02	SAz-2	MX-80	S65	B75	MSU	GBM-Na	GBM-Ca	Nontronite	Beidellite BDI-1	Saponite MCA-C	Saponite B64	Illite IdP-2	Kaolinite
	2.0	0.4	4.2	1.0	5.1	0.9	8.7	13.3	2.0	2.0	1.0	16.0	4.0	3.0		1.0
	1.3	0.1	1.1	1.0	2.0	0.2	0.6	-	1.0	3.0	-	-	3.0	1.0	7.0	
	0.4	0.6	0.0	-	2.0	0.4	0.2	2.6	2.0	3.0	-	-	7.0	-	-	-
	2.5	5.0	2.6	-	0.0	0.6	4.2	2.6	1.0	2.0	-	-	1.0	-	-	-
	93.9	91.1	87.4	98.0	89.0	96.9	80.6	79.6	92.0	89.0	95.0	84.0	85.0	96.0	93.0	99.0
	-	0.8	3.0	-	-	0.3	-	-	-	-	-	-	-	-	-	-
	-	1.9	0.4	-	-	0.2	1.3	0.6	-	-	-	-	-	-	-	-
	-	0.1	1.3	-	-	1.0	4.5	-	Tz	-	-	-	-	-	-	-
	-	-	-	-	1.9	-	-	-	2.0	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	1.5	-	-	-	-	-	-	-	-
	-	-	-	-	-	-	-	-	-	-	4.0	-	-	-	-	-
	-	0.1	1.3	-	-	0.5	4.5	-	-	-	-	-	-	-	-	-
	-	-	Tz	-	-	Tz	Tz	-	-		-	-	-	-	-	-

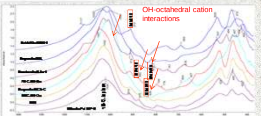
Bentonite	FEBEX	IBECO	MX-80	R02K6-F02	B75	S65	MSU
Phyllosilicates (w.t.%)	94	91	89	87	81	97	80
Smectite (w.t.%)	94	88	89	n.d.	78	94	79
Illite (w.t.%)	--	2	Tz	n.d.	1	2	Tz
Kaolinite (w.t.%)	--	--		n.d.	2	1	1
Chlorite (w.t.%)	--	--		n.d.	--	--	Tz



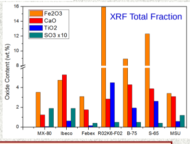


TG-DSC Curves

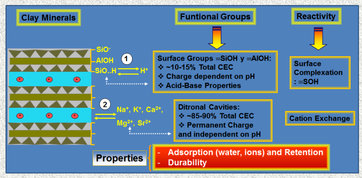




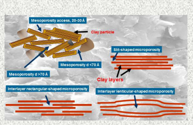
FTIR Spectra

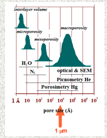


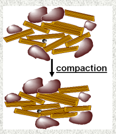
PHYSICO-CHEMICAL CHARACTERISTICS



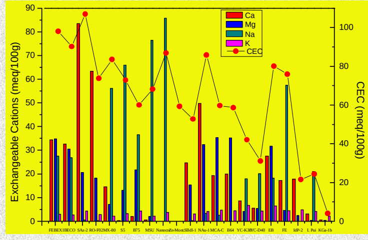
Cation Exchange Equilibria in Clays



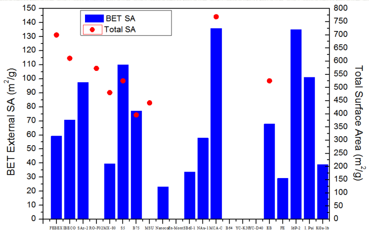




Microstructure and Textural Properties ⇒ affect ion distribution in the pore space

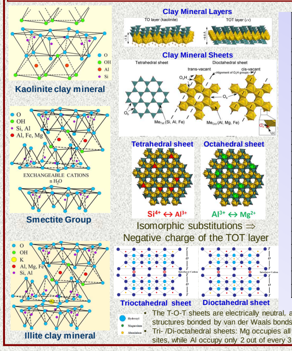


CEC is proportional to smectite content



- BET is lower for Na-smectites than for Ca-smectites
- Total surface area depends on smectite content
- Saponites have a higher BET and Total SA than montmorillonites
- Illites have a high BET surface area but a low Total SA

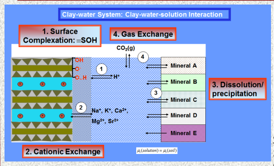
GEOCHEMICAL AND CRYSTALLOCHEMICAL COMPOSITION

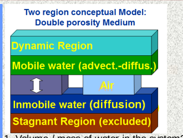


Bentonite	Origin	Structural Formulae(*)	t%	o%	Interlayer Charge	Layer Type (tetrahed.:octaed.) /Type	Di-, Tri-octahedral Sm / Cis-, Trans-vacant
FEBEX	Almería (Spain)	$(Si_{3.95}Al_{0.05})(Al_{1.37}Fe^{3+}_{0.21}Ti_{0.01}Mg_{0.49})O_{10}(OH)_2(Ca_{0.09}Na_{0.10}K_{0.07})$	15	85	0.66	2:1 / Ca-Mg-Sm	Di-oct, cis-vacant
Ibeco	Mylos (Greece)	$(Si_{3.90}Al_{0.10})(Al_{1.34}Fe^{3+}_{0.26}Ti_{0.05}Mg_{0.41})O_{10}(OH)_2(Ca_{0.10}Na_{0.06}K_{0.05})$	33	66	0.60	2:1 / Ca-Mg-Sm	Di-oct, cis-vacant
Mont. SAz-2	Arizona (USA)	$(Si_{3.93}Al_{0.07})(Al_{1.40}Fe^{3+}_{0.10}Mg_{0.50})O_{10}(OH)_2(Ca_{0.29})$	12	88	0.57	2:1 / Ca-Sm	Di-oct, Cis-v
Rockle07	Rokle deposit (Czech)	$(Si_{3.58}Al_{0.42})(Al_{0.84}Fe^{3+}_{0.65}Ti_{0.25}Mg_{0.26})O_{10}(OH)_2(Ca_{0.04}Na_{0.33}K_{0.04})$	92	8	0.46	2:1 / Ca-Sm	Di-oct, Trans-Cis-vacant
MX-80	Wyoming (USA)	$(Si_{4.00})(Al_{1.51}Fe^{3+}_{0.22}Ti_{0.01}Mg_{0.24})O_{10}(OH)_2(Ca_{0.07}Na_{0.15}K_{0.01})$	0	100	0.58	2:1 / Na, Sm	Di-oct, cis-vacant
Sabenil S-65	Na-activated (Czech)					2:1 / Na-Sm	Di-oct, Trans-Cis-vacant
B-75	Na-activated (Czech)	$(Si_{3.74}Al_{0.26})(Al_{1.15}Fe^{3+}_{0.42}Ti_{0.19}Mg_{0.22})O_{10}(OH)_2(Ca_{0.04}Na_{0.17}K_{0.11})$	72	28	0.36	2:1 / Na-Sm	Di-oct, Trans-Cis-vacant
MSU	Khakassia deposit (Russia)					2:1 / Na-Sm	Di-oct, Cis-vacant
Nanocor	Synthetic (China)		0	100		2:1 / Na-Sm	Di-oct, Cis-v
Zn-Montmorillonite	Synthetic (DE)	$(Si_{4.00})(Al_{1.64}Zn_{0.39}\ _{0.97})O_{10}(OH_{1.95}F_{0.05})(Na_{0.3})$	0	100	0.30	2:1 / Na-Sm	Di-oct, Cis-v
Beidellite (SbdI-1)	Idaho (USA)	$(Si_{3.57}Al_{0.43})(Al_{1.81}Fe^{3+}_{0.11}Mg_{0.09})O_{10}(OH)_2(Ca_{0.185}K_{0.104})$	90	10	0.47	2:1 / Ca-Sm	Di-oct, Trans-v
Nontronite (NAu-1)	Uley Graphite Mine (Australia)	$(Si_{3.49}Al_{0.51})(Al_{0.15}Fe^{3+}_{1.84}Mg_{0.02})O_{10}(OH)_2(Na_{0.53})$	99	1	0.53	2:1 / Ca-Sm, Fe-rich	Tri-oct
MCA-C	Toledo (Spain)	$(Si_{3.74}Al_{0.26})(Al_{0.26}Fe^{3+}_{0.14}Mg_{2.31})O_{10}(OH)_2(Ca_{0.16}K_{0.65})$	62	38	0.39	2:1 / Sm, Mg-Ca-saponite	Tri-oct
B-64	Germany					2:1 / Sm, Mg-Ca-saponite	Tri-oct
YC-K38	Kallo (Belgium)	$(Si_{3.86}Al_{0.14})(Al_{1.42}Fe^{3+}_{0.33}Mg_{0.20}Ti^{4+}_{0.02})O_{10}(OH)_2(Na_{0.13}K_{0.29})$	33	67	0.37	2:1 / Na-Sm	Di-oct, Trans-vacant
YC-D40	(Doel, Belgium)	$(Si_{3.93}Al_{0.07})(Al_{1.32}Fe^{3+}_{0.37}Mg_{0.25}Ti^{4+}_{0.02})O_{10}(OH)_2(Na_{0.12}Ca_{0.04}K_{0.22})$	18	82	0.41	2:1 / Na-Sm	Di-oct, Trans-vacant
GBM-Ca (EB Exp.)	Almería (Spain)	$(Si_{3.96}Al_{0.04})(Al_{1.44}Mg_{0.38}Fe^{3+}_{0.14}Fe^{2+}_{0.05})O_{10}(OH)_2Ca_{0.16}Na_{0.07}K_{0.04}$	9	91	0.44	2:1 / Ca-Sm	Di-oct Sm/ Cis-vacant
GBM-Na (FE Exp.)	Almería (Spain)					2:1 / Na-Sm	Di-oct Sm/ Cis-vacant
Illite du Pui	Pui (France)	$(Si_{3.52}Al_{0.48})(Al_{1.17}Fe^{3+}_{0.49}Mg_{0.33})O_{10}(OH)_2(Ca_{0.04}Na_{0.12}K_{0.64})$	57	43	0.84	2:1 (I)	Dioctaedral
Kaolinite (KG-1b)	Georgia (USA)	$(Si_{1.94}Al_{0.05})(Al_{2.01}Fe^{3+}_{0.001}Fe^{2+}_{0.003})O_{10}(OH)_2(Mg_{0.03}K_{0.001})$	--	--	0	1:1 (Kaol)	Dioctaedral

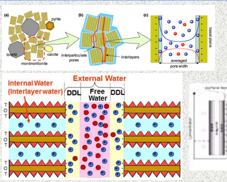
(*) Some of the described structural formulae are from bibliography

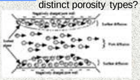
PORE WATER COMPOSITION: Salinity, Free water composition and Anion Accessible Porosity

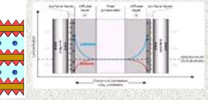




1- Volume / mass of water in the system?
2- Distribution of the water volume in distinct porosity types?





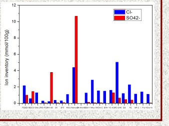


Pore water chemistry extracted by Squeezing

Bentonites	Febex 28.2% w.c.	Ibeco 28.9% w.c.	MX80 25.6% w.c.
Pressure (MPa)	25	25	25
pH	7.3	7.8	8.0
I (M)	0.27	0.19	0.33
Cl (mg/L)	6600	2800	1100
SO_4^{2-} (mg/L)	2600	4300	9300
Br^- (mg/L)	12	5	<5
NO_3^- (mg/L)	143	58	1200
HCO_3^- (mg/L)	125.66	175.68	--
Alk. (meq/L)	2.06	2.88	n.d.
Si (mg/L)	14	8.5	<0.8
Na (mg/L)	3200	2400	4900
K (mg/L)	34	43	59
Ca (mg/L)	649	380	278
Mg (mg/L)	591	312	146
Sr (mg/L)	11	4	6.8
Fe (mg/L)	≤0.15	<0.38	<0.8
Al (mg/L)	0.27	<0.38	<0.8
pCO_2 (bar)	-2.37	-2.7	--

Aqueous Extracts

Accessible Porosity	MX-80	FEBEX	Ibeco
Cl porosity/Water Porosity	0.24	0.42	0.27



CONCLUSIONS

Different properties and compositional characteristics of the clay materials analysed have a direct relationship with the mechanisms of colloid formation from compacted bentonite during bentonite erosion. The clay characteristics that seems to affect the colloid characteristics and stability behaviour depends on: a) the total smectite content in the sample, b) the Na content in the exchange complex (**Na** vs. Ca), c) the type of cation at octahedral sites (**Al** vs. Mg or Fe) the location of the layer charge (tetrahedral vs. **octahedral** defect of charge location), d) the type of sheet in octahedral sites (**dioctahedral** vs. trioctahedral), (d) the salinity of pore water (**low** vs. high), i.e., DDL behaviour; f) the presence of kaolinite and other accessory minerals, such as oxides; which prevent erosion.

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[1] Missana, T., Alonso, U., Fernández, A.M., Schatz, T.; R. Červinka, J. Gondolli, ÚJV Řež, a. s. U., 2015. Final Report on the effects of the water chemistry and clay chemistry on erosion processes. Belbar Project. Deliverable 2.7., 25 pp. EC Contract Number: 295487; [2] Alonso, U., Missana, T., Fernández, A.M., 2015. Comparison of erosion behaviour of different clays. This Volumen.

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Ciemat Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

BELBaR

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