

Detailed Description of the Crystal-Chemical Properties of Clays

Clays

Mg-Clays, stevensite and sepiolite from the Madrid basin

Sepiolite, with the idealized structural formula $[\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4] \cdot 8\text{H}_2\text{O}$, was supplied by TOLSA S.A., commercialized under the PANSIL100® (PAN100) brand and extracted from mineral deposits from the Madrid basin. PAN100 is a mineral compound of approximately 95% sepiolite (<5% feldspars and quartz; <1% calcite). Sepiolite is a natural sheet silicate of fibrous morphology. The nature of the tetrahedral sheets is completely siliceous. The octahedral sheet is completely magnesian, and both have a low number of isomorphic substitutions, creating virtually no permanent layer charge. Octahedral sheets have continuity in the elongation direction of fibres, but the tetrahedral sheets exhibit a periodic apical oxygen inversion in the perpendicular direction, which produces discontinuity in the octahedral layer. This discontinuity opens up structural channels called zeolitic tunnels with the capacity to adsorb small molecules of approximately $0.37 \times 1.06 \text{ nm}$ (Álvarez et al., 2011; Ruiz-Hitzky, 2001). Sepiolite is considered a special clay due to its fibrous structure, which is responsible for its unique physicochemical properties.

Stevensite was supplied commercially by TOLSA, S.A. under the MINCLEAR N100® brand (>90% stevensite, 5% dolomite, <5% quartz and feldspars). Stevensite belongs to the trioctahedral smectites group, where octahedral positions are occupied by divalent cations. Its structure is ideally derived from the structure of talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, conversely to dioctahedral smectites, in which trivalent cations occupy two-thirds of the possible octahedral positions and are derived from the pyrophyllite structure, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. Smectites are sheet silicates characterized by two siliceous tetrahedral sheets around an octahedral sheet (T–O–T or 2:1) with total planar continuity-forming sheets (Güven, 2009). In stevensite, the permanent layer charge arises from the existence of divalent cation vacancies ($\text{M}^{+0.5}[\text{Mg}_{2.5}\square_{0.5}\text{Si}_4\text{O}_{10}(\text{OH})_2] \cdot n\text{H}_2\text{O}$; \square : vacancy; M^+ : cation counterion for permanent negative layer charge) (i.e., (Benhammou et al., 2005).

Di(Al)-octahedral smectites and illite

Smectites' group layer structures usually have a permanent charge due to isomorphic substitution in tetrahedral and octahedral sheets. Di-octahedral species are common. Four Al-dioctahedral smectites have been used in the study: a beidellite type, two high-charge montmorillonites and one low-charge montmorillonite.

Beidellite (ideally $\text{M}^{+0.5}[(\text{Al}, \text{Fe(III)})_3\text{Si}_{3.5}\text{Al}_{0.5}\text{O}_{10}(\text{OH})_2] \cdot n\text{H}_2\text{O}$) is the main component of the fine fraction of clay minerals included in arkose sandy sediments around the Universidad Autónoma de Madrid. This mineral has been used in sand amendments with or without complementary bentonites for studying its use as an impermeable barrier (Ruiz et al., 2012). This mineral has a permanent charge due to the isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral layer. This feature allows the clay to have high interaction with ionic groups on the surface. Montmorillonite isomorphic substitutions are located mainly in octahedral sites occupied by trivalent cations where a small amount of Mg^{2+} is substituted for Al^{3+} or Fe^{3+} . MX-80 bentonite (in the paper it is referenced as LC Mnt) supplied by AmColl (American Colloid Company) (95% smectite, 5% quartz and feldspars) contains montmorillonite with $\text{M}^{+0.35}[(\text{Al}_{1.55}, \text{Fe(III)}_{0.20}, \text{Mg}_{0.25})\text{Si}_{3.90}\text{Al}_{0.10}\text{O}_{10}(\text{OH})_2] \cdot n\text{H}_2\text{O}$ (Fernández et al., 2014), a low-charge montmorillonite ($\text{M}^+ < 0.374$, Emmerich et al., 2009 criterion), and has Na^+ as the dominant interlayer cation. FEBEX (in the paper HC Mnt; >95% smectite, <5% albite, cristobalite, quartz) and MMT-Chile (in the paper HC Mnt LFe) bentonites (>95% smectite, <5% Pyrophyllite, albite, heulandite, quartz) are mainly high-charge montmorillonites ($\text{M}^+ > 0.426$), $\text{M}^{+0.50}[(\text{Al}_{1.35}, \text{Fe(III)}_{0.20}, \text{Mg}_{0.45})\text{Si}_{3.95}\text{Al}_{0.95}\text{O}_{10}(\text{OH})_2] \cdot n\text{H}_2\text{O}$ and $\text{M}^{+0.55}[(\text{Al}_{1.35}, \text{Fe(III)}_{0.10}, \text{Mg}_{0.60})\text{Si}_{4.00}\text{O}_{10}(\text{OH})_2] \cdot n\text{H}_2\text{O}$;

the MMT-Chile with a low iron ideal montmorillonite composition and Na⁺ as the main interlayer cation; and FEBEX with Ca–Mg–Na 1/2-1/3-1/5 interlayer cations. The origin of both bentonites is the dacitic–andesitic volcanic rock alteration in Cabo de Gata (Almería, Spain: Caballero et al., 2005) and the Andes mountain range, 400 km east of Santiago de Chile.

Illite is also a 2:1 di-octahedral sheet silicate with dehydrated K⁺ (not exchangeable) within the interlayer region (K⁺ 0.8–1.0/O₁₀(OH)₂ basis). This gives the mineral a rigid character, due to a strong ionic bond that holds the layers together and prevents water from entering the interlayer, as occurs in smectites (Chang et al., 2012). Red clay from Carboneros (Bailén, Jaén), supplied commercially by Cerámica Comercial Bailén S.A., has been used. This clay is more than 70% illite, 20% quartz and feldspars and 5% dolomite (Vázquez and Jiménez-Millán, 2004).

Although most of the described clay minerals have active interlayer surfaces for cationic exchange, all of them have variable charges that are pH-dependent on the surface of hydroxyl groups or on the edge of the particles with non-compensated bonds (Si-O•••, Al-O•••, Mg-O•••). This situation causes positive or negative charges as a function of protonation (low pH) or deprotonation (high pH) of the groups in the mineral edge (Kraepiel et al., 1998).

Iron oxyhydroxides, Ferrihydrite and goethite

Two-line ferrihydrite and goethite was synthesized as described elsewhere (Li et al., 2011 and Luengo et al., 2006). Either 5 or 1 M NaOH solution was slowly added to 0.4 M Fe(NO₃)₃ up to a final pH of approximately 7.0. The resulting sample suspension was allowed to age for 22 h at 20 °C in the dark. It was then repeatedly washed with ultrapure water until the conductivity was less than 10 µS·cm⁻¹. The aged suspension was freeze-dried and ground to obtain a reddish-brown powder. A similar procedure was followed for goethite synthesis. In fact, NaOH volumes were slowly added to a 0.4-M Fe(NO₃)₃ solution to a final pH of 12. The resulting suspension was allowed to age for 72 h at 65 °C in the dark, and after several washes, the resulting dialyzed suspension was freeze-dried and ground to obtain a yellowish powder (Yunta et al., 2013).

Calcined sewage sludge

This sludge is a residue from the calcination of sludge from a sewage water treatment plant. It is a dried and crushed material (sphere < 2 mm) calcined at 800 °C as the residue of the sludge gasification process (Sánchez et al., 2007). XRD analysis showed that this is an amorphous glass with quartz and feldspar impurities.

All the materials were characterized by means of X-ray diffraction powder patterns, confirming their crystalline properties and estimating their crystal size (Figure 2). The mineralogical analysis of the samples was carried out by XRD using a PANalytical X'Pert PRO diffractometer with Ge (111) as the primary monochromator. This procedure allowed for the selection of CuK_{α1} radiation analysed with an X'Celerator detector. The samples were registered in the range of 3° < 2θ < 70°, with a step size of 0.0167° and a counting time of 100 s for each step. The samples were analysed by the random powder method. Specific surface areas were determined by nitrogen gas adsorption at 77 °K in a Gemini V Micromeritics® equipment after degassing the powdered sample under N₂ flow for 18 h at 90 °C (UNE 22-164/94).

Note: citations are referenced in the paper.