# INVESTIGATION OF HUNGARIAN MONTMORILLONITES AND PREPARATION OF ALUMINA-PILLARED MONTMORILLONITES

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Pillared clays (PILCs) are microporous materials. The preparation procedure of pillared clays is based on the intercalation of large metal cations between the clay sheets by an ion exchange procedure. A second step converts these pillar precursors into rigid oxide particles that are tightly bonded to the clay layers.

These inorganic oxide pillared clays offer good properties as ion exchangers and ion selective membranes, protective coatings, and sensors; they can be used in pollutant scavenging and waste management, acid or non-acid catalysed organic reactions.

A variety of pillaring species is known including organic cations, organometal pillars, metal oxide sols, metal complexes, and polyoxycations. Some mixed pillars are used for forming specific active sites in the material. The intercalation of clays with polyoxycations of $Al^{3+}$ resulted in one of the first types of inorganic PILCs. This is also the most investigated pillared layered clay up till now. The main pillaring agent that is responsible for the 10 Å interlayer distance in alumina-pillared clays, is the $Al^{3+}$ oligomer $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, briefly $Al_{13}$ = Keggin ion. This polyoxycation is the result of a controlled hydrolysis of aluminium salts.

Different kinds of natural samples were taken of the Hungarian bentonite deposits Mád, Koldu and Istenmezeje for preparation and investigation of alumina-pillared interlayered materials. The morphological appearance of Koldu and Mád bentonites is very similar, while Istenmezeje bentonite has a little bit different features: the most jagged, frilled surface of the adhered bunches and the least grain size. For pillaring two different kinds of concentrations of clay suspensions were prepared, namely 10 g/l and 15 g/l.

A pillaring solution of Keggin ion was added to the clay suspensions of raw bentonite and also between the sodium saturated montmorillonites sheets, and after mixing for a few hours the suspensions were filtered and washed. The successfully intercalated montmorillonites with aluminium-polyoxycations were settled to the bottom of beaker, and the sediments looked as a velvet and were softly light. In the intercalated products were detected well discernible colour and textural differences for lower (10 g/l) and higher (15 g/l) concentration clay suspensions. The intercalated materials were air dried at ambient temperature on a glass plate and subsequently calcined at 350°C for 3 hours, and also at 500°C for 2 hours in air.

Resulting alumina-pillared clays were characterised by X-ray diffraction measurements. A basal spacing around 18.5–19.5 Å indicated right away that alumina pillaring occurred since the layer thickness of an anhydrous smectite layer is 9.5 Å and the size of the $Al_{13}^{7+}$ Keggin ion is about 9 Å. The d(001) values of Istenmezeje intercalated montmorillonites were the lowest, the calcined samples had line broadening, as well as the basal peaks of clays were partly returned. Calcined Mád clay samples display the least decrease in d-spacing indicating the best pillared samples for sodium form, both for lower and higher concentrations of clay suspension. Mád and Koldu pillared layer structures absolutely fulfil the minimum criteria of pillared material according to the X-ray. Pillared samples prepared by 15 g/l concentration of clay suspension disclose lower d-spacing loss for all clay than 10 g/l at 500°C temperature. Furthermore, thermal analysis, and BET surface area measurements were applied to examine the new materials. Alumina-pillared Hungarian clay minerals (Na-Mád and Na-Koldu) have specific surface areas around 150–200 $m^2/g$ that nicely meets the accepted requirements. The alumina pillaring was successful in highly concentrated clay suspensions (10 and 15wt%) and highly concentrated aluminium-polyhydroxy complex solutions by simple stirring at room temperature. This method provides an economical way to synthesise alumina-pillared clays in a high scale production.

## References

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