# Chemical Stability of Aluminium–Iron- and Iron-pillared Montmorillonite: Extraction and Reduction of Iron

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A substantial amount of iron(III) from Al/Fe- and Fe-pillars is (*i*) extracted by hydrochloric acid, ammonium oxalate at pH 3 and dithionite and (*ii*) reduced to $Fe^{II}$ by hydrazine vapour or liquid or dithionite, while only trace extraction and reduction was found for dithionite–citrate–bicarbonate (DCB).

Pillared clay minerals (PILCs) are layered silicates with polynuclear cationic species in the interlayers, preventing collapse of the layers. The porous structures thus obtained have higher basal spacings and Brunauer–Emmett–Teller (BET) specific surface areas than the parent minerals.[1] The synthesis of PILCs has been extensively investigated in recent years and various metals, such as aluminium, chromium, zirconium, gallium and titanium have been incorporated into the pillars.[1–5] Aluminium pillars doped with transition metals,[6–8] and bi- or multi-metallic pillars are also known.[3,9]

The properties of Fe-PILCs have been reported in several different studies with some conflicting results. Pillars of Cr or Fe are unstable under strongly acidic conditions; however, Fe incorporated into the pillars of an alumina pillared clay increases its resistance to 0.05 mol $dm^{-3}$ HCl.[10] Fe-PILCs have a good activity for the removal of metals from crude oil under high pressure conditions, and a mild hydrocracking activity.[11] Some confusion exists as to the redox activity of Fe-containing pillars. Pillars of $Fe^{III}$ can be reduced to $Fe^{II}$ and metallic Fe by $H_2$ at elevated temperatures. In this case, the Fe atoms form thin-film/pancake-shaped particles and the clay interlayers collapse. In Al/Fe-PILC, however, more $Fe^{III}$ is reduced to metallic Fe than in Fe-PILC, the interlayers remain open after reduction, and all reduced Fe is reoxidized by $O_2$ to $Fe^{III}$.[12] In a different study, involving various Al/Fe-pillared synthetic hectorites, mixed $Al_{13-x}/Fe_x$ pillars were identified. $Fe^{III}$ was slowly reducible by temperature programmed reduction with hydrogen if the pillar was Fe, but no reduction occurred if the pillar was Al/Fe.[13] The objective of the present study is to investigate the stability of Al/Fe- and Fe-pillared montmorillonite during treatment with acids, and complexing and/or reducing agents.

Two Fe-bearing clays were used in this study. The FAZA clay is a mixed Al/Fe-PILC (Al : Fe = 9 : 1) (Straton, Hi-Tec, Athens) in use as a reference PILC by the Concerted European Action–Pillared Layered Structures (CEA-PLS) group and Tx-Fe[14–16] is an Fe-PILC. The Fe contents of these materials are 4.55 and 24.8% (*m*/*m*), respectively.

The extraction results are shown in Table 1. All treatments were effective in removing Fe with the exception of dithionite–citrate–bicarbonate (DCB).[17] The ammonium oxalate method was developed as a mild treatment to remove amorphous Fe from soils and it is expected to leave crystalline phases unaffected. Table 1 shows that some Fe is removed by this method from both PILCs. DCB is a widely used technique to remove Fe oxides and oxide hydroxides from clays and soils.[17] It is based on reduction of $Fe^{III}$ by dithionite and complexation of dissolved $Fe^{II}$ by citrate. Surprisingly, this treatment was almost ineffective in extracting Fe from both PILCs. It dissolved substantially less Fe than the much milder ammonium oxalate treatment. Possibly the higher pH compared to unbuffered dithionite and/or the presence of citrate and bicarbonate contributed to the low solubility of Fe in the pillars. Unbuffered sodium dithionite was the most effective extraction agent for the Tx-Fe clay, removing as much as 25% of the total Fe. The much lower value (4%) obtained for FAZA suggests that the main part of Fe in these pillars is fixed strongly in the pillars; in other words, no isolated Fe- and Al-pillars exist, only mixed Fe/Al-pillars. As expected, treatment with either cold or warm HCl removed substantial amounts of Fe from both PILCs, but in all cases the amount was less than 20% of total Fe. Slightly higher values were obtained with warm acid and with FAZA (Table 1).

The results of $Fe^{III}$–$Fe^{II}$ reduction are given in Table 2. Both hydrazine and unbuffered sodium dithionite are known to reduce some structural $Fe^{III}$ in smectites;[19] however, DCB treatment with $N_2$ purge of the reaction mixture can result in more than 90% reduction of $Fe^{III}$ to $Fe^{II}$.[20] Table 2 shows that both vapour and liquid hydrazine reduced more than 40% of the total $Fe^{III}$ in FAZA and was also highly effective in reducing Tx-Fe. The great effectiveness of hydrazine in PILCs as opposed to smectites could be attributed to the microporosity of these clays, which allows direct contact of hydrazine molecules with $Fe^{III}$. Furthermore, the higher reduction level achieved with FAZA compared to Tx-Fe is thought to be due to the dispersed nature of the Fe atoms in the Al/Fe pillars, where a lower change in the total charge of the pillars occurs even when a high proportion of $Fe^{III}$ is reduced.

Unbuffered sodium dithionite reduced as much as 59% of the $Fe^{III}$ in Tx-Fe, which is much more than the 14% obtained for FAZA (Table 2). This suggests that the reducing agent, the sulfoxylate free radical,[21] could be eliminated by contact with Al in the pillars and thus rendered ineffective for reduction of $Fe^{III}$. Only trace amounts of $Fe^{III}$ were reduced

**Table 1** Iron extraction[a]

| Extraction | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| PILC | % Fe extracted[b] | | | | |
| FAZA | 3.6 | 4.3 | 0.3 | 9.5 | 17 |
| Tx-Fe | 6.2 | 25 | <0.1 | 5.8 | 15 |

[a] Approximately 470 mg of FAZA and 250 mg of Tx-Fe and 36 ml of following solutions were used: 1, 0.2 mol $dm^{-3}$ ammonium oxalate + 0.2 mol $dm^{-3}$ oxalic acid adjusted to pH 3, shaken for 4 h at room temp. in the dark. 2, 1 g of sodium dithionite added to water suspension of clay preheated to 80 °C and extracted for 15 min. 3, same as 2, but instead of water a mixture of 8 parts of 0.3 mol $dm^{-3}$ sodium citrate + 1 part of 1 mol $dm^{-3}$ $NaHCO_3$ was used.[17] 4, 1 mol $dm^{-3}$ HCl, shaken for 4 h at room temp. 5, 1 mol $dm^{-3}$ HCl, extracted for 15 min at 80°C. [b] Solutions were analysed for total Fe by AAS.

**Table 2** Iron reduction[a]

| Reduction | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| PILC | % $Fe^{III}$ reduced[b] | | | |
| FAZA | 48 | 60 | 14 | 1.4 |
| Tx-Fe | 20 | 39 | 59 | 0.4 |

[a] Approximately 20 mg of PILCs were reduced: 1, by hydrazine vapour in a desiccator at room temp. for 20 h. 2, in 36 ml of hydrazine for 20 h at room temp. 3, 100 mg of sodium dithionite added to 36 ml of water suspension of the PILC and purged with $N_2$ for 2 h.[20] 4, same as 3, but instead of water a mixture of 8 parts of 0.3 mol $dm^{-3}$ sodium citrate + 1 part of 1 mol $dm^{-3}$ $NaHCO_3$ was used. [b] Solid reaction products were analysed for $Fe^{II}$ and total Fe by 1,10-phenanthroline method.[18]

by DCB in both PILCs, which also accounts for the low Fe dissolution observed from this treatment. The lack of reducing activity of DCB, in contrast to sodium dithionite alone, must imply that citrate and/or bicarbonate play some role in inhibiting the reduction of $Fe^{III}$ in the pillars. Further experimental work is required to understand the mechanism involved.

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