

NOTE

AN AMORPHOUS PRODUCT OF COMPLEX COMPOSITION IN A SILURO-DEVONIAN SILTSTONE

Recently, Cole *et al.* (1981) reported that the difficulty in operating the upstream valves in diversion tunnels of an Australian dam could have arisen partly from alkali–aggregate reaction and partly from the instability of the siltstone and sandstone used in the concrete. During preparation of samples for mortar-bar testing, it was noticed that the crushed siltstone contained aggregates coated with white-grey clay, and unusual thin translucent flakes about 0.1 mm thick and up to 5 mm in diameter released by crushing. The purpose of this note is to describe the flaky material and to compare its properties with those of the clay coating on the siltstone aggregates. These materials could have been involved in the alkali–aggregate reaction that had occurred in the concrete.

Experimental

The siltstone, a marine deposit of Siluro-Devonian age, was sampled from a depth of ~60 m. In hand specimen the rock was dark grey with a very weakly developed fissile foliation and it also showed some paler grey bands several millimetres wide. Thin sections of the uncrushed rock and of the flaky material were made for petrological examination. An inclusion-free portion of a flake was X-rayed with a Unicam single-crystal camera before and after dipping in dilute HCl. The clay coating of the 10–20 mm aggregates was brought into a water suspension ultrasonically, and used in K⁺- and Mg²⁺-saturated forms for X-ray diffraction (XRD) studies. A portion of the clay was refluxed with dimethyl sulphoxide (Garcia & Camazano, 1968) to check for the presence of kaolinite. Samples of flakes and rock fragments were mounted on a carbon stub for scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX). The flaky material and the clay were also examined by transmission electron microscopy (TEM) and selected-area electron diffraction (SAED).

Results

Siltstone petrography. Thin sections of the siltstone showed a slightly recrystallized argillaceous mosaic containing finely divided ‘sericitic’ minerals intergrown with weakly birefringent clay. Quartz particles were finer (0.04 mm) in the darker argillaceous band and coarser (0.08 mm) in the paler bands, which also contained muscovite flakes up to 0.05 mm long. Opaque minerals were concentrated in narrow bands up to 0.1 mm wide. The sections also showed very small amounts of plagioclase feldspar and narrow bands of non-birefringent translucent material about 0.1 mm wide.

The XRD pattern of the rock powder (<75 µm) indicated large amounts of quartz, mica, chlorite and possibly kaolinite, and very small amounts of plagioclase feldspar. The

clay fraction gave identical XRD patterns in the air-dried and glycerolated states, and also after heating at 300°C for 1 h, with sharp reflections at 14.30, 10.05, 7.10 (strongest), 5.00 and 4.72 Å. The 7.10 and 4.72 Å peaks disappeared after heating to 600°C for 1 h, indicating a non-expanding, Fe-rich chlorite (14.30, 7.10 and 4.72 Å) and mica/illite (10.05 and 5.00 Å). Refluxing with dimethyl sulphoxide indicated that kaolinite was absent.

Examination of the clay material by TEM showed well-defined particle shapes which gave strong diffraction patterns typical of crystalline clay minerals. The scanning electron micrographs of the clay on rock fragments (Fig. 1) showed platy particles (labelled M) and very fine particles (arrowed), both of which gave high K contents on EDAX spectra (Figs 2A,D) and were thus assumed to be mica/illite. The smaller and more rounded particles (labelled C) were the chlorite component of the clay, since they contained much less K and

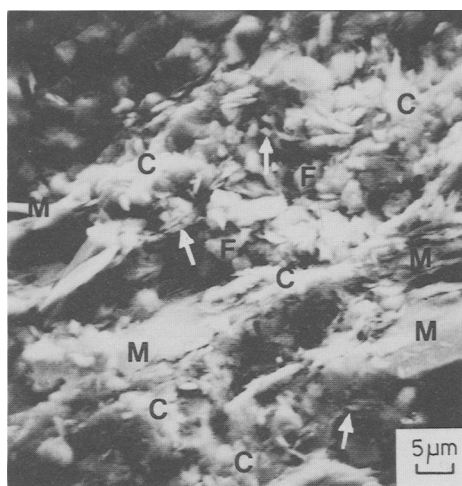


FIG. 1. Scanning electron micrograph of clay particles coating the crushed siltstone aggregates.
M = mica/illite; C = chlorite, F = feldspar.

much more Fe and Mg (Fig. 2B) compared to the mica/illite. Feldspar particles (labelled F) were observed occasionally and contained large amounts of Na (Fig. 2C).

Amorphous flaky material. Portions of the flakes which were free from large inclusions extinguished under crossed nicols, indicating that they were either amorphous or isotropic, or isotropic sections through anisotropic material. Flakes containing inclusions showed numerous fine crystals, mainly 0.01-mm quartz particles, and occasional clusters of plagioclase feldspar and mica flakes about 0.08 mm in diameter.

Initially, the inclusion-free flakes gave a weak but distinct XRD pattern for calcite. However, this pattern disappeared after the same flake was dipped in dilute HCl, indicating that the base material was amorphous to X-rays. The amorphous component appeared under TEM to consist of particles with no definite shape but which appeared to be welded together with some fine inclusions; no electron diffraction pattern was given. The inclusions contained Ca, Ti, Fe and Mg, as well as the Al and Si that constituted the amorphous matrix (Fig. 2E).

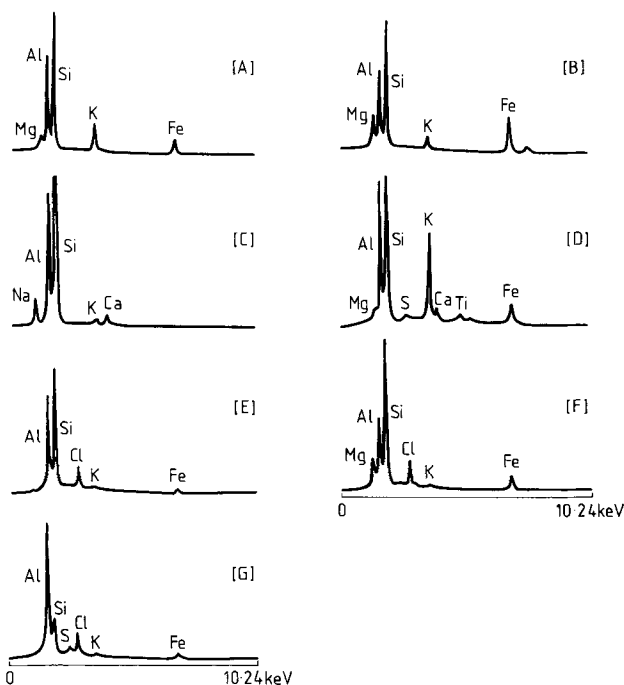


FIG. 2. EDAX spectra of the clay materials coating the silstone aggregate (A, B, C, D) and of the amorphous component (E, F, G). The spectra are for large mica plates (A); chlorite particles (B); plagioclase feldspar (C); fine mica (D); flake matrix (E); particles on the flake surface (F, G).

In contrast to the particles in Fig. 1, the amorphous component appeared very fragmented under the SEM. Individual particles having the composition of chlorite were observed, but with K content and Al/Si peak ratios (Fig. 2F) much smaller than those of the clay materials. Other chlorite-like materials were much lower in Fe than the actual clay in the rock. A few particles had compositions similar to the Na-rich plagioclase (Fig. 2C). Whereas some particles smaller than $2\ \mu\text{m}$ were composed largely of Al (Fig. 2G), other larger particles ($5\text{--}10\ \mu\text{m}$) contained mainly Si.

Discussion

Examination under the petrological microscope indicated the existence of flaky material in the uncrushed rock, and XRD and SAED methods confirmed its amorphous nature.

The SEM and EDAX results showed a greater range of composition in the amorphous component than in the clay material. Compositional ranges in the amorphous component were similar to those of materials resulting from leaching and decomposition of the clay material, suggesting that the two are related and that the former is possibly an altered form of the latter.

The slight metamorphism indicated by petrographic examination could have altered the clay materials deposited on the bedding planes of the rock, under pressure and shear, to the amorphous component. However, the temperature would not have risen high enough

to produce typical metamorphic minerals. The rock was sampled from below the water table where the aqueous reducing conditions are also favourable for leaching of K and Fe from mica and chlorite. Loss of structure due to a few hours of grinding has been documented for montmorillonite (Cicel & Kranz, 1981) and for muscovite (Mackenzie & Milne, 1953). Similar results were also found by Reay (1981) for a number of minerals including chlorite. If the amorphous component formed from the clay minerals in the siltstone, its loss of structure could have been caused by some kind of grinding action.

Conclusions

Although the origin of the amorphous component and the process of its formation is uncertain, its composition suggests that it may be related to, and possibly formed by, the alteration of the clay minerals in the siltstone. The amorphous nature of this Si-containing material would render it potentially reactive to alkali and, therefore, undesirable in concrete, where an alkali-silica reaction could occur.

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