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Cr^{+6}, Cr^{+3}, $Fe^{+3}$and Se in natural ettringite group minerals

E. Sokol, S. Kokh, Yu. Seryotkin, O. Gaskova, and O. Kozmenko

V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russian Federation (sokol@igm.nsc.ru, +7383 3332792)

Ettringite is a very important mineral in cement technology and an essential agent in immobilization of potentially toxic compounds (Cr, As, Se). Being stable at pH=9-13 and T<90˚C, ettringite is very rare in natural occurrences. It is, however, widespread in the peculiar sequence of ultrahigh-temperature ambient-pressure calcareous combustion metamorphic rocks of the Hatrurim Formation (Israel and Jordan) derived from slightly phosphatic chalks and marls annealed by burning methane at 1200-1350˚C. The mineralogy of certain combustion metamorphic rocks is comparable to that of cement clinker. Namely, the mineral assemblages of brownmillerite-ye'elimite-larnite ($\pm$ fluorellestadite, mayenite, gehlenite, hatrurite, perovskite, spinel) rocks are similar to calcium sulfoaluminate cement (CSA). Some CM rocks contain up to 570 Cr, 100 Se, 445 Zn, and 28 U (in ppm) while As is under 30 ppm. Hydrothermal alteration of these rocks produces ettringites of different compositions, which also occur as a main phase in veins (calcite, aragonite, vaterite, thaumasite, tobermorites, afwillite, other CSHs, opal, brucite, and portlandite) that crosscut the Hatrurim sequence.

Pure sulfate ettringite is a rock-forming mineral in veins while its Cr^{+3}, Cr^{+6}, and Fe^{+3}-substituted analogs are of quite a rare occurrence. They exist as independent partings or fill vugs, and are easily spotted in the field with, correspondingly, bright lilac, greenish-yellow, and greenish colors. The yellow color was the most intense in Cr^{+6}–bearing ettringite from the veins that cut metamorphic rocks rich in brownmillerite, Fe-spinel, and Ca ferrites, containing Cr^{+3} as an impurity. Perfect canary yellow prismatic ettringites are restricted to small vugs inside monolith blocks and may be define as secondary ettringite.

Octahedral Al^{3+}can fully substitute for Cr^{3+} (up to 1.99 apfu) to produce bentorite, with the empirical formula $(Ca_{5.91}Mg_{0.01}Na_{0.01})[Cr_{1.99}Al_{0.01}Si_{0.02}](OH)_{12}(SO_4)_{3.01}$*(19.9)$H_2O$. Fe^{3+} substitution for $Al^{3+}$is limited (up to 3.3 wt% Fe_2O_3). The principal replacement of sulfate with oxyanions include $(CrO_4)^{2-} \rightarrow (SO_4)^{2-}$ (up to 0.35 apfu Cr) and $(CO_3)^{2-}$+ $(SiO_4)^{4-} \rightarrow 2(SO_4)^{2-}$ (up to 0.66 apfu Si). In some crystals the substitution reactions are simultaneous and attendant with incorporation of Se (up to 640 ppm). The empirical formula is $(Ca_{5.99}Mg_{0.01}Na_{0.01})[Al_{1.46}Si_{0.44}](OH)_{12}(CrO_4)_{0.35}(CO_3)_{0.45}(SO_4)_{2.00}$*16.7$H_2O$.

Relatively wide spread of ettringite within the Hatrurim complexes and its ability to structurally incorporate both Cr^{3+} and CrO_4^{2-} allows one to consider its behavior in prolonged geological processes with regard to chromium immobilization. Cr^{+6}-bearing ettringite preserves the best inside monolith rocks similar to low-permeable natural CSA clinkers. This is just the system in which ettringite has the highest Cr^{+6}immobilization efficiency. Natural ettringite never incorporates large amounts of Cr^{+6} (the highest (SO_4):(CrO_4) $\sim$ 7.6), though, according to modeling, the equilibrium concentration of total soluble Cr reaches in this case 2.7310^{-2}mol/kg H_2O. As the monoliths break down during road quarrying and become exposed to rainfall, Cr^{+6}-bearing ettringite begins to decompose and dissolve immediately. This appears to be the most likely mechanism responsible for Cr^{+6}releases from CM rocks and for current precipitation of chromatite ($CaCrO_4$)