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Note

Formation of mixed Mg Al hydroxides with interlayer nitrate and carbonate ions

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In a recent study[1] of the formation of spinel, Mg Al_2O_4, by thermal treatment of mixed Mg and Al hydroxides, Selim et al.[1] remarked on the formation of an apparently new species when mixed solutions of Mg and Al nitrates in the ratio Mg: Al = 1:2 were treated with ammonia. The phase in question gave a *d*-spacing of 8.67 Å and the suggestion was made that it was "probably a hydrated spinel".

On the basis of current knowledge[2,3], the phase in question is likely to be a hydroxy nitrate resembling the hydroxy carbonate mineral hydrotalcite, $Mg_6Al_2(OH)_{16}\cdot CO_3\cdot 4H_2O$, which consists of a brucite-like hydroxide layer $Mg_6Al_2(OH)_{16}$ with resultant charge +2 and interlayer CO_3^{2-} ions. Many similar hydroxy anion materials are known probably with various $R^{2+}:R^{3+}$ ratios, and various interlayer anions. Taylor[3] has reviewed these structures. Gastuche et al.[2] especially studied the products obtained with mixed Mg and Al chlorides by addition of NaOH. The products varied with the atom percent Al in the following manner

0–~ 15 atom % Al,	$Mg(OH)_2$ + complex hydroxide
~15–~ 33 atom % Al,	complex hydroxide
~33– 100 atom % Al,	complex hydroxide + $Al(OH)_3$

With long periods of dialysis in water, a carbonate product was obtained due to dissolved CO_2.

The Mg:Al ratio used by Selim et al.[1], chosen to yield a spinel after heat-treatment, with 67 atom % Al lies midway between the mixed-phase limits of 33 and 100 atom % Al. The product therefore is likely to be a mixture of $Al(OH)_3$ and the complex hydroxide with 33% Al, 67% Mg. A likely formula is $[Mg_4Al_2(OH)_{12}]^{2+}X^{2-}\cdot n\,H_2O$ where X^{2-} may be $2(NO_3)^-$ when mixed nitrate solutions are used, or CO_3^{2-} if the product is carbonated.

RESULTS AND DISCUSSION

X-ray data

We have repeated the experiments of Selim et al.[1] using nitrate solutions and ammonia to precipitate the product. We have also used NaOH with essentially the same results. After washing the products by centrifugation to remove excess OH, Na or NH_3, and NO_3, with a diphenylamine test for NO_3 ions, samples were dried in air at 60 °C and at 110 °C. X-ray diffraction confirmed the presence of $Al(OH)_3$ as bayerite and a mixed hydroxide with a basal spacing of about 8.5 Å (Selim et al.[1] gave 8.6 Å). Samples treated with 0.1 N Na_2CO_3 solution for 1 week at 60 °C gave a product resembling hydrotalcite with a spacing of 7.59 Å. The diphenylamine test confirmed the release of nitrate ions from the initial product.

IR data

The initial product gave an absorption peak near 1380 cm^{-1} with shoulders at about 1360 and 1400 cm^{-1}. The carbonate product gave a broader peak near 1350 cm^{-1} with a shoulder near 1400 cm^{-1}. These are presumably the ν_3 vibrations of the NO_3 and CO_3 anions, respectively. The ν_3 peak intensity of the NO_3 product is about twice that of the CO_3 product in agreement with the replacement of $2(NO_3)^-$ ions by one CO_3^{2-} ion.

Structures

We can speculate on the basal spacings of the products. If the mixed Mg, Al hydroxy material in the carbonate form has the composition $Mg_4Al_2(OH)_{12}CO_3 \cdot nH_2O$, which is based on the data of Gastuche et al.[2], the brucite-like layers will have two sheets of close-packed hydroxyls each with 6(OH) per formula unit and a spacing of about 2.2 Å between OH planes, and $CO_3 + n\,H_2O$, i.e. $(3 + n)$ oxygens will occupy interlayer positions. If these interlayer oxygens are in apposition to the hydroxyl ions[3,4], the overall basal spacing will be about 2.2 + 2.7 + 2.7 = 7.6 Å in agreement with the observed value. Replacement of each CO_3 group with two NO_3 groups will give $(6 + n)$ interlayer oxygens per formula unit. Whether this larger number of interlayer oxygens occupies two planes of NO_3 groups and water molecules, or the NO_3 groups have a non-planar arrangement is uncertain. If the oxygen ions are entirely in close-packed arrangements with the hydroxyl ions, the net spacing would be about $4 \times 2.2 = 8.8$ Å, whereas the observed value is near 8.5 Å. A non-planar arrangement therefore is possible. In the present context, however, it is a reasonable conclusion that the larger spacing of the nitrate product as compared with the carbonate product arises from twice as many anions involved.

CONCLUSION

The unidentified phase mentioned by Selim et al.[1] is not a hydrated spinel but belongs to the group of brucite-like hydroxide structures with various interlayer anions and water molecules.

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