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Report:

Layered double hydroxides (LDH) are a group of minerals (hydrotalcites) and synthetic solids. They consist of layers of edge-sharing metal hydroxide octahedra hosting divalent metal cations like, Ni²⁺, Zn²⁺, Co²⁺ and Cr²⁺. In up to 1/3 of the cationic centers, the divalent cations are replaced by Al³⁺ [1,2]. The resulting net positive charge of the hydroxide sheets is counterbalanced by hydrated anions in the aqueous interlayers, responsible for the anion exchange properties.

In comparison with simple metal hydroxides, LDH phases have a significantly lower solubility at relevant geochemical conditions. Therefore, formation of such phases plays an important role in reducing the toxicity of metals and radionuclides in e.g., soils, sediments and nuclear waste repositories [3].

Voegelin et al. examined the solubility of pure Zn and Ni LDHs as well as of mixed Zn-Ni LDH phases in column experiments under acidic conditions [4]. When only Zn was present, 95% of the retained Zn was leached at pH 3. In contrast, only 23% of the retained Ni was leached in experiments with Ni alone. When both Zn and Ni were present, 90% of the retained Zn and 87% of the retained Ni were released. EXAFS analysis performed at room temperature revealed that the LDH phases in the Zn experiment had been completely dissolved, while the LDH phase formed in the Ni experiment was still present. The intention of our study was to investigate whether or not differences in the short-range structure are responsible for these differences in solubility.

EXPERIMENTAL. Three samples were prepared: 1) pure Zn²⁺ LDH with 1/3 Al³⁺ inclusion, 2) pure Ni²⁺ LDH with 1/3 Al³⁺ inclusion, 3) mixed LDH with 1/3 Zn²⁺, 1/3 Ni²⁺, 1/3 Al³⁺. The Zn and Ni K-edge spectra were collected in transmission mode at 20 K using a closed-cycle He cryostat.

RESULTS. The measured EXAFS spectra had a much lower noise than previously published LDH spectra due to the reduction of the thermal components of the Debye Waller factor (Fig. 2). For the pure ZnAl and NiAl LDH the difference of metal distances is in line with the ionic radii of Zn²⁺ (0.74

Å) and Ni²⁺ (0.69 Å) (Table 1). For the mixed ZnNiAl LDH the coordination distances around Ni and around Zn are again in line with the respective ionic radii. The metal shell distances, however, are intermediate between those of pure NiAl and ZnAl LDH, suggesting an even distribution of Ni and Zn in the hydroxide layers and the absence of a significant clustering of ZnAl hydroxide or NiAl hydroxide regions (Fig. 1). The Al backscattering atoms fitted for the first metal shell are confirmed by the Morlet waverlet method [5]. Using the refined FEFF-Morlet method [6], we could also confirm that Al atoms are present in the third metal shell (≈ 6.2 Å), but not in the second metal shell (≈ 5.2 Å), suggesting an even, charge-balanced distribution of Al³⁺ in the mixed-metal hydroxide layers for all investigated LDH phases.

CONCLUSIONS. All structures revealed an even distribution of 3d-metals and Al. No significant structural differences were found between the binary Ni-Al and Zn-Al LDH on one hand, and ternary Zn/Ni-Al LDH on the other hand. Hence, the differences in solubility are not caused by structural differences.

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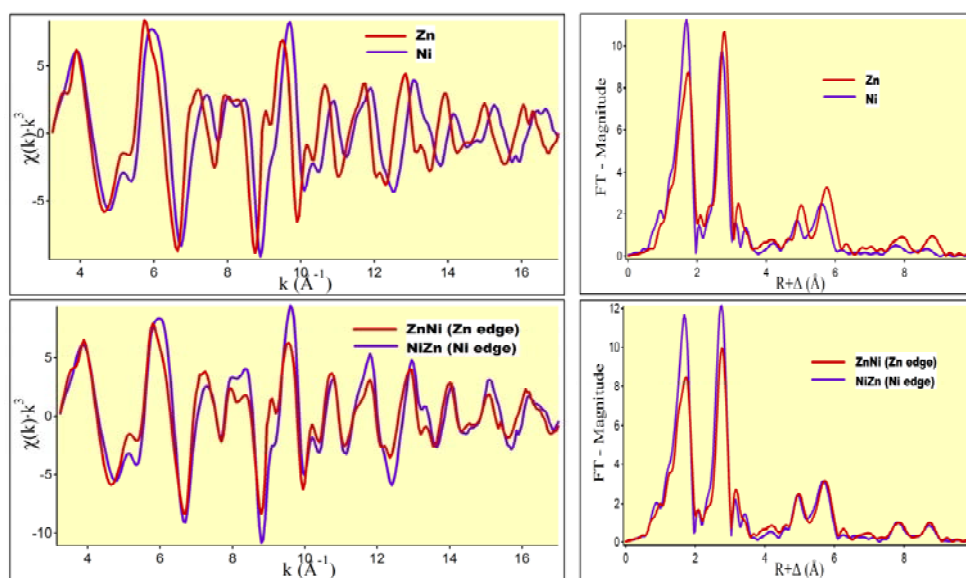


Fig. 1. EXAFS spectra and corresponding Fourier transform of the pure Zn-Al and Ni-Al LDH (above) and of the mixed ZnNi-Al LDH (below) measured at Zn-K and Ni-K edges, respectively.

Table 1. EXAFS fit result of ZnAl LDH, NiAl LDH, and a mixed ZnNiAl LDH phase.

Sample	Edge	O			1 st metal			1 st Al			2 nd metal			3 rd metal + MS		
		CN	R	σ^2	CN	R	σ^2	CN	R	σ^2	CN	R	σ^2	CN	R	σ^2
Zn	Zn	6.0	2.08	0.0072	3.6	3.07	0.0048	2.8	3.06	0.0036	4.6	5.32	0.0062	12.8	6.21	0.0095
ZnNi	Zn	5.7	2.08	0.0070	3.1	3.05	0.0050	1.9	3.03	0.0023	4.9	5.30	0.0063	11.5	6.18	0.0093
ZnNi	Ni	5.7	2.05	0.0042	5.4	3.07	0.0040	3.9	3.11	0.0028	2.2	5.29	0.0027	9.4	6.15	0.0083
Ni	Ni	5.6	2.05	0.0045	1.6	3.04	0.0027	1.0	2.91	0.0020	1.9	5.23	0.0036	8.4	6.10	0.0092