

Supplementary material

CO₂ Mineralization of Steel Slag into Vaterite for High-Efficiency Zn²⁺ Removal and Upcycling into Hydrozincite

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Supplementary Figures

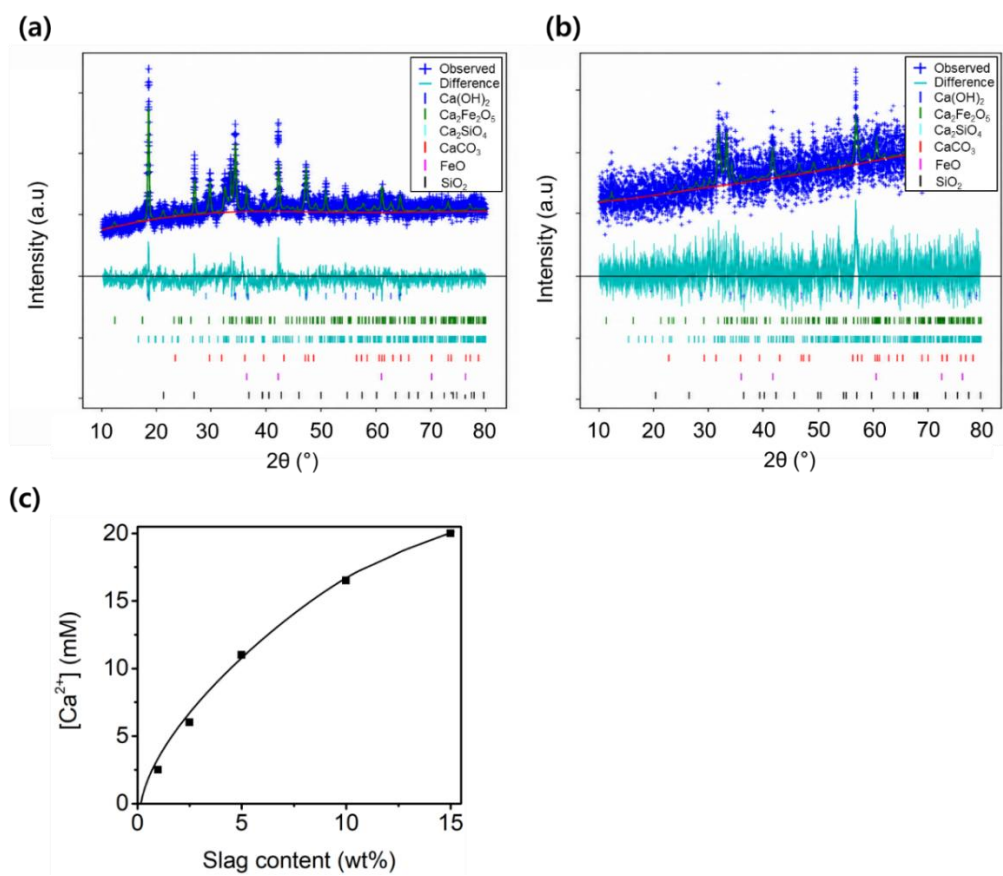


Fig. S1. Rietveld refinement of the XRD patterns of (a) raw steel slag and (b) leached steel slag. (c) Ca^{2+} concentration in the leachate as a function of slag content.

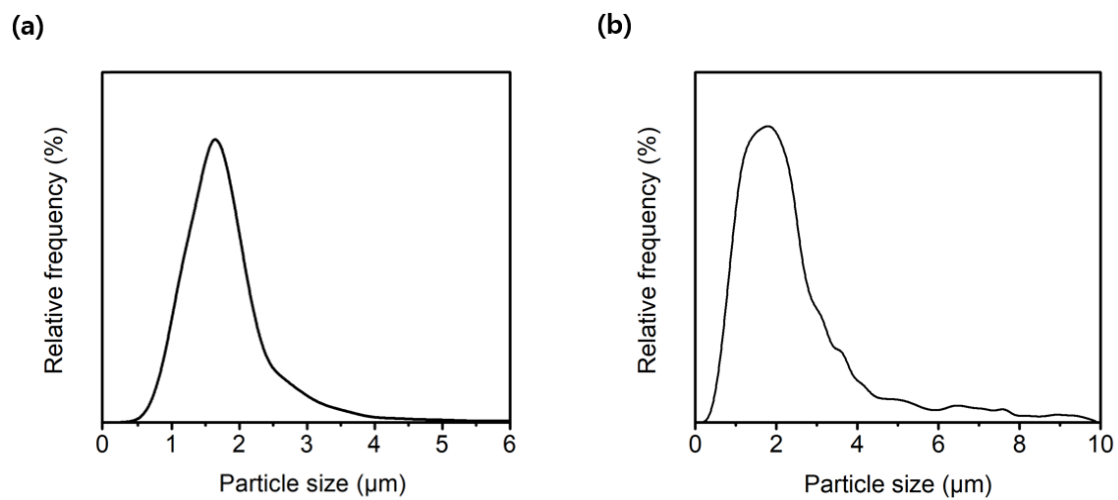


Fig. S2. Particle-size distributions of CaCO₃ precipitates synthesized in the presence of (a) *L*-arginine (vaterite) and (b) *L*-lysine (calcite), showing average particle sizes of approximately 1.7 and 2.0 μm, respectively, as determined from optical microscopy (OM) images.

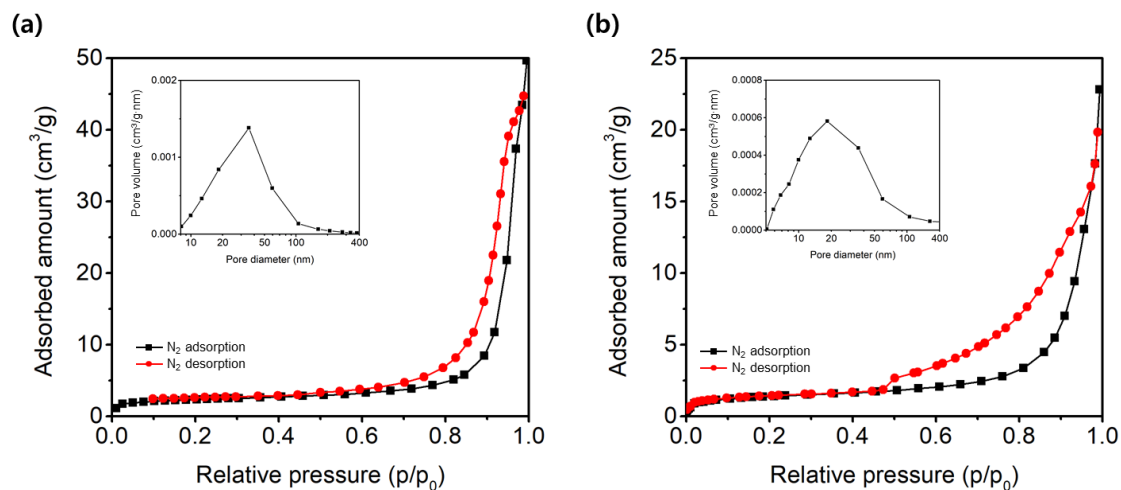


Fig. S3. N₂ adsorption–desorption isotherms and BJH pore-size distributions of (a) *L*-arginine-derived vaterite and (b) *L*-lysine-derived calcite synthesized from steel-slag leachate. The BET specific surface areas of vaterite and calcite were 11.19 and 1.95 m²/g, respectively.

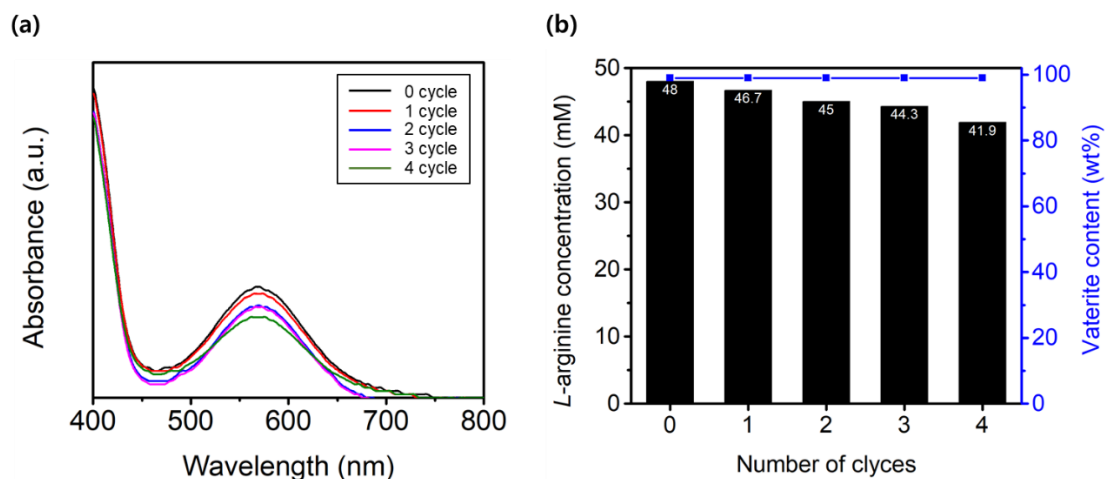


Fig. S4. (a) UV-Vis absorption spectra of the ninhydrin-derivatized *L*-arginine solutions recovered after each reuse cycle and (b) *L*-arginine concentration and vaterite content over successive reuse cycles. Black bars represent *L*-arginine concentrations, and blue symbols represent the vaterite content of the resulting precipitates.

After each synthesis cycle, the solution recovered by solid-liquid separation was directly reused for the subsequent cycle, and the *L*-arginine concentration was determined by the ninhydrin colorimetric method based on the absorbance at 570 nm. The *L*-arginine concentration decreased from 48.0 to 41.9 mM after four reuse cycles, corresponding to 87.3% of the initial concentration, while the vaterite content remained approximately 99%. These results indicate that the recovered *L*-arginine solution retained its ability to direct vaterite formation.

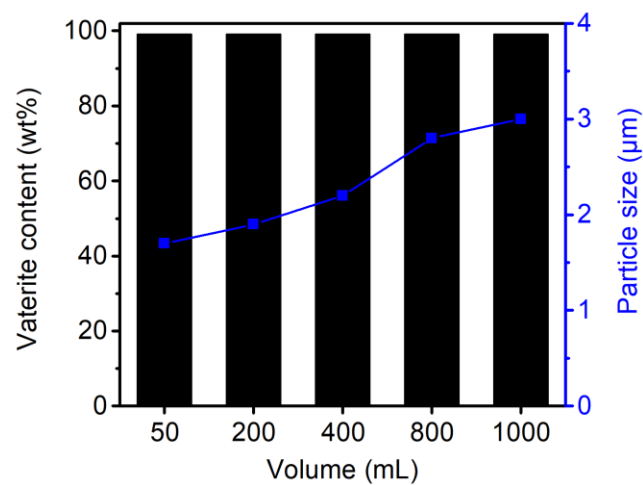


Fig. S5. Vaterite content and average particle size of CaCO_3 precipitates synthesized at reaction volumes ranging from 50 to 1000 mL. Black bars represent vaterite content, and blue symbols represent average particle size.

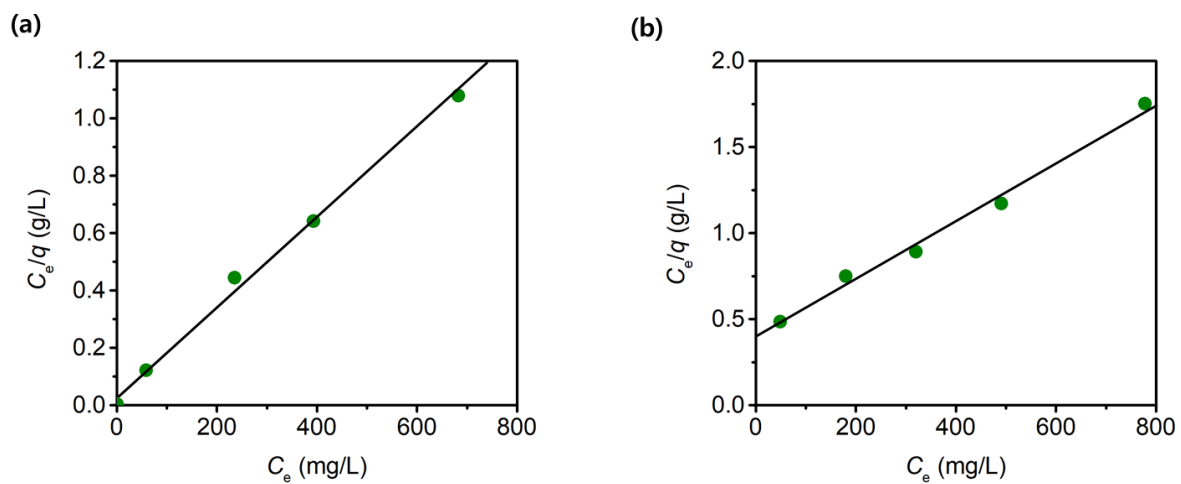


Fig. S6. Linearized Langmuir plots (C_e/q versus C_e) of the concentration-dependent Zn^{2+} removal data for (a) vaterite and (b) calcite after 2 h of reaction. Symbols represent experimental data, and solid lines represent the linear fits.

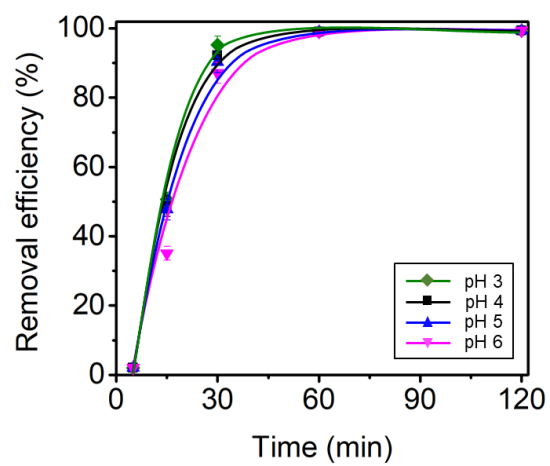


Fig. S7. Time-dependent Zn²⁺ removal by vaterite at initial solution pH values of 3-6.

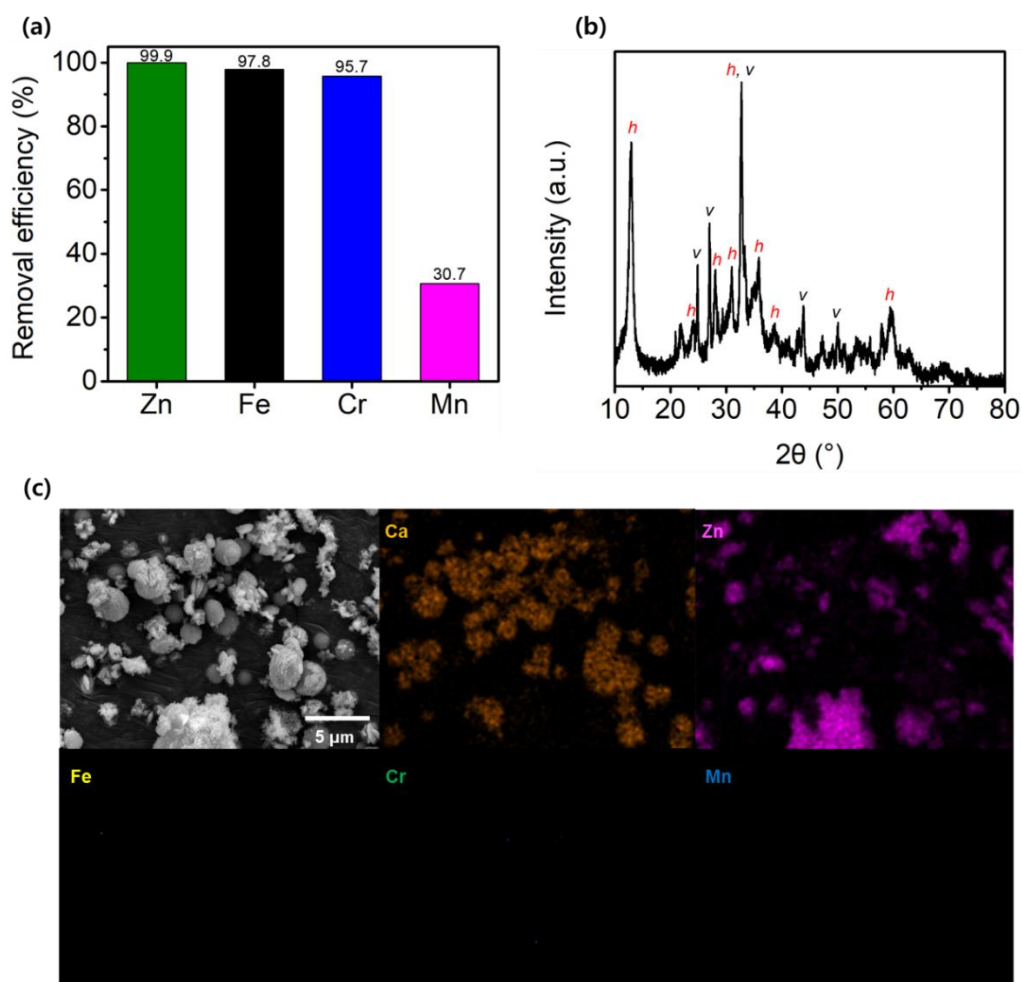


Fig. S8. Metal removal and characterization of the recovered solids after treatment of a synthetic wastewater containing 1000 mg/L Zn^{2+} and 10 mg/L each of Fe^{3+} , Cr^{3+} , and Mn^{2+} at an initial pH of 3.0. (a) Metal removal efficiencies after 120 min at a vaterite loading of 2.0 g/L. (b) XRD pattern of the recovered solids, where *v* and *h* denote vaterite and hydrozincite, respectively. (c) SEM image and corresponding EDS elemental maps of Ca, Zn, Fe, Cr, and Mn.

After 120 min, the residual Zn^{2+} concentration was ≤ 1 mg/L, corresponding to a removal efficiency of $\geq 99.9\%$, while the removal efficiencies of Fe, Cr, and Mn were 97.8%, 95.7%, and 30.7%, respectively (Fig. S8a). XRD analysis identified hydrozincite together with residual vaterite in the recovered solids (Fig. S8b). The corresponding EDS maps showed clear Ca and Zn signals, with a Ca/Zn atomic ratio of approximately 0.95 in the analyzed region, whereas Fe, Cr, and Mn signals were weak or not discernible because of their low contents in the recovered solids (Fig. S8c). These results demonstrate effective Zn^{2+} removal accompanied by hydrozincite formation in the multimetal solution.

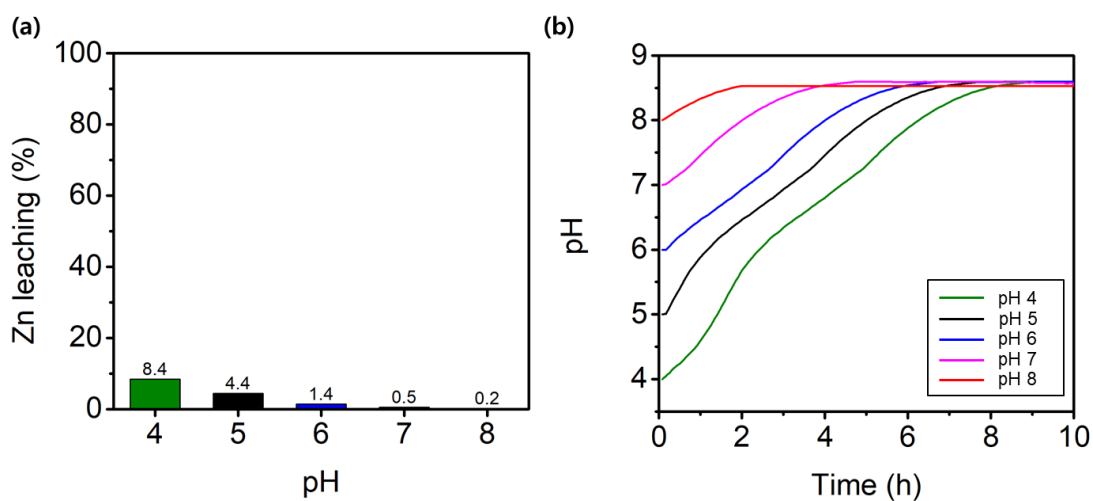


Fig. S9. Leaching behavior of recovered hydrozincite showing (a) Zn leaching percentages at initial solution pH values of 4-8 and (b) corresponding changes in solution pH during the leaching tests.

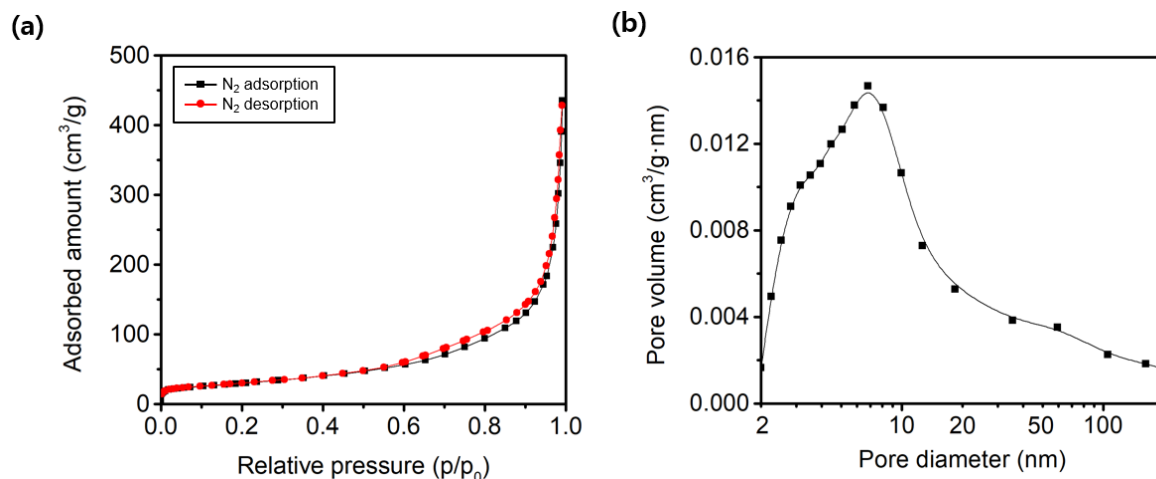


Fig. S10. (a) N_2 adsorption-desorption isotherms and (b) BJH pore-size distribution of nanoflower-like ZnO derived from the spent hydrozincite, revealing a high BET specific surface area of $107.8 \text{ m}^2/\text{g}$ and a mesoporous architecture.

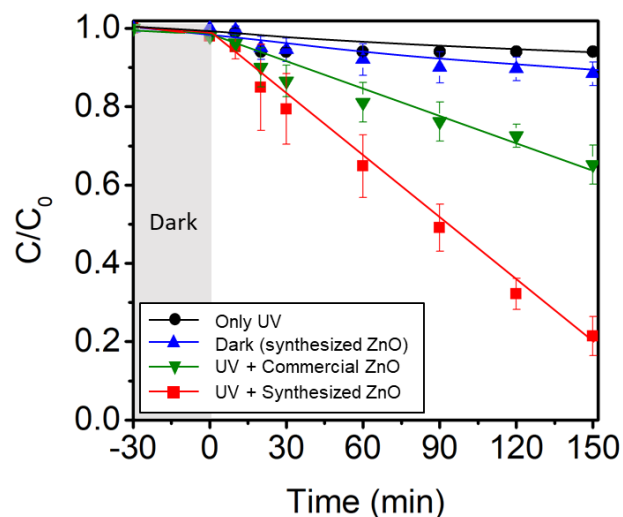


Fig. S11. Photocatalytic degradation of phenol by hydrozincite-derived ZnO and commercial ZnO under UV-visible irradiation (phenol 50 mg/L, catalyst loading 0.5 g/L). Results of irradiation without a catalyst and of hydrozincite-derived ZnO in the dark are also shown.

The suspension was stirred in the dark for 30 min before exposure to UV-visible irradiation (320-500 nm) for 150 min. Samples were collected at selected intervals and filtered to remove the catalyst. Phenol concentrations were determined by UV-Vis spectrophotometry (UV-2600, Shimadzu) at 270 nm using a calibration curve prepared from phenol standards. Commercial ZnO obtained from Samchun Chemical (Seoul, Korea) was evaluated as a reference photocatalyst under identical conditions. Hydrozincite-derived ZnO exhibited substantially higher photocatalytic activity than commercial ZnO. After 150 min of irradiation, C/C_0 decreased to approximately 0.21 for the hydrozincite-derived ZnO, compared with approximately 0.65 for commercial ZnO.

Supplementary Tables

Table S1. Elemental composition of steel-slag leachate used in this study.

Element	Concentration (mM)
Ca	16.51
Mg	<0.01
Na	0.88
K	0.20
Si	0.01
Fe	<0.01

Table S2. Parameters obtained from linearized Langmuir fitting and nonlinear pseudo-first-order fitting of Zn²⁺ removal by vaterite and calcite.

Model	Parameter	Vaterite	Calcite
Langmuir model	$q_{\max}$ (mg/g)	643.3	589.8
	K_L (L/mg)	0.049	0.004
	R^2	0.995	0.990
Pseudo-first-order model	q_e (mg/g)	200	133.6
	k_I (min ⁻¹)	0.049	0.022
	R^2	0.917	0.934

The concentration-dependent Zn²⁺ removal data obtained after 2 h were fitted using the linearized form of the Langmuir equation:

$$\frac{C_e}{q} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}}$$

where q is the Zn²⁺ removal capacity (mg/g), C_e is the residual Zn²⁺ concentration after 2 h (mg/L), $q_{\max}$ is the fitted asymptotic removal capacity (mg/g), and K_L is the empirical fitting constant (L/mg). $q_{\max}$ and K_L were obtained from the slope and intercept of the C_e/q versus C_e plot, respectively (Fig. S6 and Table S2). The equation was used to describe the concentration dependence of Zn²⁺ removal.

The time-dependent Zn²⁺ removal data were fitted using the pseudo-first-order equation:

$$q_t = q_e[1 - \exp(-k_1 t)]$$

where q_t is the Zn²⁺ removal amount at time t (mg/g), q_e is the fitted asymptotic removal amount (mg/g), and k_1 is the apparent rate constant (min⁻¹). The fitted parameters are summarized in Table S2. Both models were used as empirical descriptions of Zn²⁺ removal during mineral transformation. Nonlinear least-squares fitting was performed using the measurements at 5, 15,

30, 60, and 120 min, with q_e constrained to ≤ 200 mg/g based on the initial Zn^{2+} concentration, solution volume, and solid dosage.

Table S3. Comparison of Zn^{2+} removal capacities of the present vaterite and previously reported materials.

Material	Zn^{2+} removal capacity (mg/g)	Conditions	Reference
Hierarchical porous vaterite microspheres	587.3	25 °C, 0.5 g/L, 60 min	(Zhang et al., 2016)
Waste mollusk shells composed mainly of calcite and aragonite	526.32	pH 5.5, RT, 24 h, $C_0 = 200\text{--}1000$ mg/L	(Fernández Pérez et al., 2022)
$\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles	666.67	pH 7, RT, 120 min, $C_0 = 25\text{--}1500$ mg/L	(Rafie et al., 2024)
MnFe_2O_4 /chitosan–Schiff base nanocomposite	289.86	pH 7.5, 55 °C, 100 min, $C_0 = 50\text{--}250$ mg/L	(Alhalili and Abdelrahman, 2024)
Nano-lignocellulose/magnesium aluminum silicate polymer gel	513.48	pH 4.52, 60 °C, 160 min, $C_0 = 800$ mg/L	(An et al., 2021)
Steel-slag-derived vaterite	633	pH 6.1, RT, 120 min; $C_0 = 100\text{--}1000$ mg/L	This study

References

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