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THERMODYNAMIC RESPONSE OF SOLUBLE AND INSOLUBLE HEAVY METAL SPECIES IN SOILS TO EXTERNAL PERTURBATIONS

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Introduction

The thermodynamic behavior of soluble and insoluble heavy metal species in acidic soils under external perturbations, including changes in pH, temperature, and chemical influx, is analyzed, with particular emphasis on phase distribution, transformation pathways, and stability under varying environmental conditions. The primary focus lies on the response of multicomponent heterogeneous systems to such disturbances through the lens of chemical thermodynamics [1]. A theoretical framework based on complex chemical equilibria and Gibbs energy variation is employed to assess buffering phenomena involving both solid (mineral) and aqueous phases. The ability of buffer systems to resist changes in their composition when subjected to the influx of chemical substances of natural or anthropogenic origin that shift the equilibrium is referred to as buffering capacity [2]. Understanding the mechanisms and extent to which contaminants disperse or diminish over time is crucial. Additionally, managing heavy metal ion concentrations in natural environments can be approached by examining how the system reacts to variations in factors that influence pM, the negative logarithm of metal ion activity. Simply put, this involves determining the system capacity to buffer changes in pM. The term pM is defined as $-\log[M]$, where $[M]$ represents the equilibrium concentration of the metal ion M^{n+}, similar to how pH is defined as $-\log[H^+]$. This paper aims to investigate the thermodynamic behaviour and buffering capacity of heavy metal species, both soluble and insoluble, in acidic soils subjected to external perturbations such as changes in pH, temperature, and chemical influx. The focus is on understanding phase distribution, transformation pathways, and stability within multicomponent heterogeneous systems by applying chemical thermodynamics principles. Using a theoretical framework based on complex chemical equilibria and Gibbs energy variation, the study assesses how mineral and aqueous phases buffer against disturbances that alter metal ion equilibrium concentration (pM). Ultimately, the work seeks to elucidate the mechanisms governing the dispersion and attenuation of contaminants, thereby informing strategies for managing heavy metal concentrations in natural environments.

Results and Conclusions

Soil buffering capacity has been revealed when increased amounts of toxic metals do not correspond to greater accumulation in plants, highlighting the soil varied response to different elements and resulting in diverse toxic thresholds. A single soil can display distinct buffering behaviors depending on the metal involved. The capacity of soils to retain heavy metals as acidity rises (pH decreases) depends on their initial pH and inherent buffering properties. Unlike single-phase systems governed by homogeneous equilibria, soil buffering arises from complex heterogeneous equilibria that regulate thermodynamic parameters such as concentration, temperature, and pH. The effective buffering range, defined by the *pM* value at which buffering is strongest, can shift with changes in the proportion of secondary solid phases. Buffering related to mineral ions is further enhanced by proton exchange and complex formation reactions in the aqueous phase. A straightforward evaluation method based on tabulated solubility data for sparingly soluble compounds has been developed to quantify these effects. The complexity of heavy metal speciation, including transformations, interactions among metals and species, and their binding to soil and mineral phases, significantly influences bioavailability. Heterogeneous buffering differs fundamentally from classical aqueous buffering, and ecosystems with low buffering capacity may struggle to maintain stable equilibrium conditions, potentially leading to environmental degradation. Moreover, mixtures of solid-phase species can produce not only additive but also synergistic effects, strengthening overall buffer action. This thermodynamic framework improves understanding of natural attenuation processes in groundwater through complexation and precipitation, enabling prediction of reaction conditions and reversibility. It demonstrates that ligands forming stable complexes with solid-phase ions enhance buffering in heterogeneous systems and can be applied to study buffer actions involving newly formed solid phases in natural waters. Quantitative models derived from this work provide original mathematical expressions for estimating mineral buffer capacities, showing that buffering is a complex function of solubility, equilibrium composition, and mineral stoichiometry. Ultimately, these insights offer valuable tools to predict soil composition and reactivity changes under increasing anthropogenic pressures, advancing knowledge in soil science, ecological stability, and environmental management. The approach also holds potential for application in other natural multicomponent systems such as surface waters and sediments.

References

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