Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.33790

Speciation of Nickel and Cobalt during Fe(II)-Mediated Birnessite Transformation

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The accumulation of anthropogenic CO_2 intensifies global warming, driving the search for carbon-negative strategies to recover critical metals. Cobalt (Co) and nickel (Ni), indispensable for batteries and renewable infrastructure, are mainly hosted in laterite deposits within iron and manganese (oxyhydr)oxides. To address this challenge, we applied Fe(II)-catalysed recrystallisation and reductive dissolution as an environmentally friendly extraction route. Unlike high-pressure acid leaching, this method efficiently releases Co/Ni from goethite and hematite at ambient temperature (25 °C) and circumneutral pH (~7.5). Yet, the role of Fe(II) in mobilising Ni and Co from birnessite (δ-MnO_2)—another key Ni/Co-bearing host in laterites—remains poorly understood. In this study, synthetic Co/Ni-incorporated birnessite was subjected to controlled Fe(II) reductive dissolution, which substantially accelerated the concomitant release of Ni and Co. Post-reaction X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) revealed mineralogical transformations, confirming birnessite reductive dissolution and secondary Fe(oxyhydr)oxide formation. These findings elucidate trace-metal cycling in Fe(II)-rich, redox-active systems and inform carbon-negative strategies for critical metal recovery from laterites. By clarifying reaction pathways and guiding process optimisation, this work supports the development of environmentally friendly technologies to secure critical metals essential for the global energy transition.