

# Summary

Built heritage is confronted by extensive challenges in a rapidly changing society and climate. Salts are one of the main causes of stone weathering and are understudied yet critical for conservation management strategies. Ion concentrations in porous materials result from various sources such as groundwater, rainwater, atmospheric, biological, or internal material contamination. Over time, these ions are transported to the surface and deposited at the drying front, where they can crystallize into various solid forms, expanding in volume and exerting pressure on their surroundings. Cycles of crystallization and dissolution, and (de)hydration can lead to material deterioration. Moreover, salt mixtures play a significant role in exogenous processes in geomorphology, planetary research, and industrial processes. Yet, most studies have focused on binary systems. To bridge this knowledge gap, this dissertation explores representative ion mixtures commonly identified in weathered stone materials, including sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ). These ions were analyzed in 11,412 drill samples from 338 historic sites with building materials showing signs of salt decay. This extensive dataset allowed for a more accurate calculation of ion equilibrium, enabling the correct identification of salt content and further investigation into the behavior of common salt mixtures through modeling and experimental verification.

One of the main issues in analyzing ion mixtures is interpreting the derived ion balance due to analytical uncertainties and undetected ions, leading to disequilibrium between anions and cations. Thus, corrections are necessary to achieve electrical neutrality for a scientifically accurate evaluation. This dissertation introduced methodological improvements in ion balance calculations, enabling a more precise interpretation of the available salt mixtures. The complete dataset and optimized charge balance calculation method were made available open-source to promote scientific community involvement. Furthermore, based on this dataset, commonly occurring mixture compositions were identified, enhancing our understanding of ions that influence mixture behavior. The corrected ion data also serve as input for thermodynamic modeling, providing insights into salt behavior using the ECOS/Runsalt model, a tool for analyzing the crystallization and dissolution behavior of salt mixtures under different climatic conditions. Specific terminology was recommended, and guidelines on how to use the model and interpret its output were detailed, emphasizing the model's limitations and providing solutions.

The research identified commonly occurring salt mixtures in Belgian architectural heritage, thereby enhancing insight into their behavior and contribution to material deterioration. The results revealed that 92% of the samples, contained at least five ions, including sodium, potassium, nitrate, chloride, magnesium, and calcium or sulfate. Furthermore, 14 common salts were identified and four frequently occurring salt mixtures. Their critical relative humidity values for crystallization/dissolution were identified, providing important insights for experimental research into stone weathering and understanding modeling and salt weathering processes under changing climatic conditions. Moreover, innovative combined analytical techniques such as Environmental Scanning Electron Microscopy (ESEM), Dynamic Vapor Sorption (DVS), Raman Spectroscopy, X-ray Diffraction (XRD), and time-lapse micrographs enabled detailed analysis of the crystallization kinetics of salts under changing relative humidity. The kinetics of crystallization of salt mixtures under various conditions were analyzed over time, showing the effects of relative humidity and mixture composition on crystallization and dissolution behavior, and establishing a correlation between the kinetics and the rate of change of relative humidity. These findings were linked with the results of the thermodynamic model and were confirmed using various analytical techniques.

The combination of results and new techniques introduces significant contributions to determining phase changes over time under different realistic climatic conditions and to the overall understanding of salt crystallization processes. Additionally, a comparison between modeled predictions and experimental outcomes validated the ECOS/Runsalt model's effectiveness and highlighted pitfalls that enhance reliability in predicting salt behavior. The overall results provided new insights into salt-related weathering processes, including identifying critical relative humidity values and crystallization/dissolution times for frequently occurring salts and mixtures, informing conservation efforts. The research provides specific implications for the conservation of built heritage by suggesting targeted management strategies based on specific environmental and material conditions. The findings are crucial for the preservation of built heritage and understanding salt deposition and dissolution mechanisms in general.