



Influence of ion exchange processes on salt transport and distribution in historic sandstone buildings



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ABSTRACT

Crystallisation of salts in the pores of stone is a major concern in the preservation of heritage buildings, monuments and sculptures, but the mechanism of transport and distribution of salts is still not properly understood. The fractionation and distribution of salts in the porous matrix has, in building material research, conventionally been attributed to the solubility and concentration of salts present in the groundwater. We propose another mechanism contributing to the control of the salt distribution based on the interaction of ions in the salt solution with the charged mineral phases within the stone. The transport of mixed salt solutions was studied in laboratory simulated flow-through experiments on two fluvial sandstones – a Permo-Triassic red bed sandstone and a Carboniferous sandstone, both from the UK. The experiments were carried out under non-evaporative conditions, eliminating the possibility of solubility-dependent crystallisation. The results indicate that the process of ion exchange significantly controls the transport of ions in the pores and leads to fractionation of solutes in the course of transport even in the absence of evaporation and crystallisation. The sandstones behave like a chromatographic column and retention of various ionic species is significantly controlled by ion exchange processes. A quantitative estimation of cation exchange capacity (CEC) indicates that sandstones with higher CEC have greater influence on retention and fractionation of salts in the course of capillary transport than those with lower CEC. Simple scoping calculations using a geochemical modelling code and the ion exchange properties based on those determined in the laboratory experiments, demonstrate that ion exchange can have a significant effect on mineral precipitation during evaporation.

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1. Introduction

It has been noted that salts are transported to different locations in porous building materials resulting in heterogeneous spatial distributions of salt (Arnold, 1982; Arnold and Zehnder, 1990, 1991). These inhomogeneous distributions are a very important factor in stone decay due to crystallisation, as the damage is related to the location of crystallisation (Rodríguez-Navarro and Doehne, 1999). The crystallisation can take place at the surface (efflorescence) and/or within the pores below the surface of the stone (subflorescence). The transport and distribution within the porous network is generally considered to be a function of surface evaporation and solubilities of the salts present in the water. However, the processes that govern the transport and spatial distribution

of salts in the context of historic buildings have not been thoroughly investigated.

The development of the fractionated distribution of salts within a building stone is usually explained as the result of the sequential crystallisation of salts as the water gradually advances through the stone and evaporates as it does so. Thus the crystalline phases are deposited in sequence according to their respective solubilities, while the most soluble solutes are concentrated in the remaining solution (Arnold, 1982; Arnold and Zehnder, 1990, 1991; Matteini, 1991). This preferential precipitation of different salt phases from salt solution leads to fractionation, forming spatial sequences of different salts.

However, there is another possibility that is rarely discussed in the context of building materials – the effect of ion exchange. Ion exchange will give rise to a chromatographic effect in the migration of ions, and this could in principle strongly affect the distribution of saturation states, either increasing or decreasing the degree of saturation. Perhaps Wendler and Snelthage (1988, cited in Schäfer and Steiger, 2002) were the first to investigate cation

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exchange capacities (CECs) of weathered building stone and noted significant differences between CEC of weathered and unweathered zones. Schäfer and Steiger (2002) compared various techniques of CEC determination in building stone and also observed that the CEC in weathered stone is much less than that of unweathered stone, though this will not necessarily always be the case as weathering can increase the proportion of clays present. However, in these studies CEC measurement was used as an indicator of chemical weathering and partial dissolution of clays and other colloidal size minerals due to acid attack, and it appears that there has been no research to study the role of ion exchange processes in salt transport through building stones. Accordingly, the study described here was devised to determine the effect of ion exchange on ion distributions as water flows through building stones to ascertain the potential importance of ion exchange in the spatial distribution of salt crystallisation.

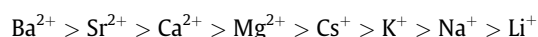
2. Cation exchange and preferential retention

2.1. Introduction

Many varieties of sandstone contain an appreciable percentage of clasts with large surface areas that have a significant capacity to exchange ionic constituents attached to their surfaces. These clasts can be detrital or authigenic mineral grains. They are often inorganic, sometimes amorphous (uncrystallised or poorly crystallised) and mostly composed of clay minerals and metal oxides and hydroxides (Freeze and Cherry, 1979). The imperfections/ionic substitutions within the crystal lattice and reactions at the particle surface result in a net positive or negative charge of the crystal lattice. This charge imbalance is compensated by a surface accumulation of ions of the opposite charge (the ‘counterions’) that form as a layer of exchangeable composition. Though almost all particles will have some excess surface charge, the most important for ion exchange are those with large surface areas. The nature of the surface charge is sometimes a function of pH. At low pH in oxides for example, a positively charged surface prevails whereas at high pH a negatively charged surface develops.

Ion exchange is usually taken to mean the phenomena associated with the presence of the excess charge on solid surfaces, with any specific bonding of solute to surface being referred to as ‘sorption’. Often in practice it is difficult to separate the results of the two processes, and the surface interactions of the major aqueous species are assumed, as here, to be associated with ion exchange.

In ion exchange the selectivity or affinity of ions for the solid surface is governed by the structural and charge properties of ions. A typical order of decreasing selectivity (affinity to exchange sites) of common cations depending on the above mentioned conditions is expressed as (Blatchley and Thompson, 2010):



Cation exchange capacity (CEC) measurement is a common practice in soil science, geochemistry, hydrogeology, etc. and there are many standard methods for CEC determination. Almost all of them follow the same principle – to measure the exchangeable cations by a displacement method. A number of solutions, for example ammonium acetate and barium chloride, have been used for displacing exchanged cations: the latter are then summed to provide an estimate of CEC (Bohn et al., 2001; White, 2006).

2.2. Quantifying cation exchange reactions

Several different models have been proposed to describe cation exchange reactions based on the assumption that the mineral surface has a constant total CEC at a given pH and the exchange

reaction is stoichiometric and reversible. Cation exchange selectivity or the preference of the exchange phase for one cation over another is described by, for example, Appelo and Postma (2005):

$$mA^{n+} + nBX_m = mAX_n + nB^{m+} \quad (1)$$

$$K_{A/B} = \frac{[AX_n]^m [B^{m+}]^n}{[BX_m]^n [A^{n+}]^m} \quad (2)$$

where $K_{A/B}$ is the equilibrium constant, X represents the exchange phase of the cation and square brackets denote activities.

The cation exchange equilibrium constant describes the relative affinity of the exchanger for two considered cations. For example, in the case of a Na^+/K^+ exchange (i.e. A being Na in Eq. (1)), equilibrium constant values less than 1 would denote an affinity for K^+ greater than for Na^+ when aqueous activities of Na^+ and K^+ are equal, meaning a preference of the exchange sites for K^+ .

Unfortunately, there exists no general model for determining the activity coefficients of ions on the exchange surfaces. As a result, various ‘conventions’ are used in estimating activities of attached ions, none of which is accurate in all situations. This means that it is usually found that measured ‘equilibrium constants’, better distinguished as ‘selectivity coefficients’, vary with exchanger composition, i.e. they are not true thermodynamic constants (e.g. Essington, 2004). However, provided that the exchange compositions do not vary markedly during water movement, reasonable estimates can often, nevertheless, be obtained in practice by use of the selectivity approach (e.g. Carlyle et al., 2004).

In this research the Gaines–Thomas convention (Gaines and Thomas, 1953), one of the most commonly applied conventions, was used for estimating ion activities on exchanger surfaces. This assumes that activities of the ions attached to the surfaces can be approximated by the equivalent fraction (i.e. activity = equivalents of sorbed ion per unit mass of dry rock/CEC expressed in equivalents per unit mass of dry rock).

3. Materials and methods

3.1. Material selection and sampling

This research was conducted on freshly quarried (non-weathered) blocks of sandstone from Locharbriggs Quarry, Dumfries, southern Scotland and Stoke Hall Quarry, Grindleford, Derbyshire, England. The Locharbriggs sample is a lower Permian, red sandstone sequence of fine to medium grain-size and distinctive aeolian cross lamination. The Stoke Hall sample is medium grained, buff coloured sandstone from the ‘Millstone Grit’ of Carboniferous (Pennsylvanian) age. These particular samples were chosen because they represent two different types of sandstones used in historic buildings (red and buff coloured), and have been widely used in the UK.

The samples for flow-through experiments were cut into cylindrical cores using a water-cooled drill. The Locharbriggs samples were 20 mm long and 31.6 mm in diameter, and the Stoke Hall samples were 45 mm long and 31.6 mm in diameter. Smaller cores were used for the Locharbriggs samples as it was taking much longer to achieve full breakthrough. All the samples for the experiment were taken from the same block of stone to minimise the error due to possible variation in properties from one block to another.

3.2. Material characterisation

Examination of the mineralogy of the samples was carried out qualitatively using polarised light microscopy (PLM) and

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