



# Calcium carbonate scaling under alkaline conditions – Case studies and hydrochemical modelling



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## ABSTRACT

Calcium carbonate scaling poses highly challenging tasks for its prediction and preventative action. Here an elemental, isotopic and modelling approach was used to decipher the evolution of alkaline tunnel drainage solutions and sinter formation mechanisms for 3 sites in Austria. Drainage solutions originate from local groundwater and form their characteristic chemical composition by interaction with shotcrete/concrete. This interaction is indicated by a positive correlation of dissolved  $K^+$  and pH (up to 12.3), and a decrease of aqueous  $Mg^{2+}$  by the formation of brucite (pH > 10.5). Variability in  $Ca^{2+}$  and DIC is strongly attributed to portlandite dissolution, calcite precipitation and  $CO_2$  exchange with the atmosphere, where the  $^{13}C/^{12}C$  and  $^{18}O/^{16}O$  signatures of calcite can be traced back to the source of carbonate. The internal  $P_{CO_2}$  value is a reliable proxy to evaluate whether uptake of  $CO_2$  results in an increase or decrease of the degree of calcite saturation with a threshold value of  $10^{-6.15}$  atm at 25 °C (pH ≈ 11). Precipitation rates of calcite are highest at pH ≈ 10. Mixing of groundwater-like solutions with strong alkaline drainage solutions has to be considered as a crucial factor for evaluating apparent composition of drainage solutions and calcite precipitation capacities.

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## 1. Introduction

Calcium carbonate scaling in tunnel drainage systems can induce serious problems due to the reduction of the cross section of drainage tubes and the pollution of receiving streams by suspended  $CaCO_3$  particles and ongoing sinter formation (Dietzel et al., 2008). Both drainage systems and receiving streams have to be monitored and cleaned periodically to provide a suitable discharge of the drainage solutions and to fulfil environmental protection assignments. Cleaning of drainage tubes is accompanied by reduced tunnel transport capacities or even no passage for vehicles (e.g. trains and cars). Consequently, dealing with scaling in tunnel drainage systems is a challenging economical task for a large number of existing tunnels and an important consideration during tunnel construction, particularly for maintenance such as treatment with scaling inhibitors and mechanical cleaning tools (Girmscheid et al., 2003a,b). The cost of maintaining drainage systems of Austrian railway tunnels can be up to 40% of the total maintenance cost during the tunnel life time of 100 a (Draschitz, 2008).

In general, the formation of  $CaCO_3$  in tunnel drainage systems is induced by groundwater reacting with the hydraulic cement phases of shotcrete at the outer lining of the tunnel, the hydraulic binder used for e.g. anchor stabilization, and/or concrete used for

construction. From this point these interactions shall be collectively referred to as water–cement interaction. Soluble phases, such as portlandite ( $Ca(OH)_2$ ), are dissolved in the groundwater, which results in elevated  $Ca^{2+}$  concentrations and an alkaline environment of the drainage solutions. Although water–cement reactions are complex,  $CaCO_3$  precipitation directly at the shotcrete/concrete is mostly caused by the redistribution of dissolved inorganic C (DIC) from the groundwater induced by a pH increase. Carbonate sinter formation in the drainage system is more complicated as exchange reactions between atmospheric and aqueous  $CO_2$  as well as mixing of solutions with different chemistry have to be considered.

Former case studies have successfully used tools such as mineralogy and the chemical and isotopic signatures of carbonate sinter and reacting solutions to obtain insight into ion leaching from shotcrete/concrete, trace element sources in drainage solutions,  $SO_4$  attack of concrete and the source of carbonate precipitates (Hillier et al., 1999; Gineys et al., 2010; Marion et al., 2005; Mittermayr et al., 2012a). However there is a strong need to develop further proxies and to combine individual signatures within a multi-proxy approach to discover apparent water–cement interaction, reaction mechanisms and kinetics of  $CaCO_3$  formation and the chemical evolution of drainage solutions.

An advanced understanding of the above aspects is required essentially to prevent carbonate sinter formation by application of tailored material for tunnel construction, correct drainage system design and suitable strategy development for counteracting

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scaling. Therefore, three Austrian tunnels were selected for assessment, involving the analysis of carbonate sinter composition in the drainage system, the drainage solutions and the locally occurring groundwater. Hydrogeochemical modelling approaches are used to decipher impacts of various physicochemical parameters, individual reaction paths,  $\text{CO}_{2(\text{aq})} - \text{CO}_{2(\text{g})}$  exchange, mixing of solutions, precipitation capacities and rates for ongoing scaling.

## 2. Study area and methodology

The Grünburg (GB), Wienerwald (WW), and Koralm tunnel (KA) were selected for case studies. As a requirement local groundwater had to be available for sampling to decipher changes in its composition due to water-cement interaction, which results in individual ranges of drainage solution chemistry. Shotcrete application in all three tunnels took place between 2004 and 2007.

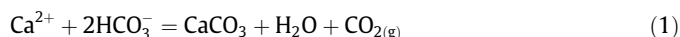
The tunnels are located within the Austrian Alps, but are related to different local geological settings. GB cuts through parts of the “Flyschzone” with a typical mixture of sandstone, limestone, siltstone, shale and mudstone. WW also penetrates geological sections of the “Flyschzone”, but with less calcareous rocks compared to GB. KA, which is still under construction, cuts through a crystalline basement of metamorphic rocks such as gneiss, quartzite and mica schist with silt- and sandstones in the Quaternary basins. However for the present task the chemical composition of the local groundwater in the respective study area is most decisive. For each case study two groundwaters were sampled from wells in the vicinity of the tunnels. Sampling of drainage solutions comprises 10, 13 and 23 solutions from GB, WW and KA, respectively. Immediately after sampling, the solutions were filtered through 0.45  $\mu\text{m}$  membranes (cellulose acetate) to avoid suspended particles remaining in the solution. Subsequent to filtration the solution was stored in gas-tight glass vessels (0.5 L) for alkalinity and in PE vessels for ion analyses (0.5 L). The sampled solutions were placed in a cool box and subsequently transferred to the laboratory for measurements. Twenty-five precipitates in total were gathered directly from the drainage system for mineralogical, chemical and isotope analyses, where 2, 11 and 12 samples are referred to GB, WW and KA, respectively.

Field data for water samples, including pH, electrical conductivity and temperature, were recorded during sampling. Alkalinity was measured in the laboratory by potentiometric titration with 0.05 N HCl within 6 h of sampling. Concentrations of cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) and anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) were determined by ion chromatography (Dionex ICS-3000) with an analytical error of  $\pm 3\%$ . The computer code PHREEQC (Parkhurst and Appelo, 1999) with the database minteq.dat was used to calculate saturation indices with respect to calcite ( $S_{\text{I}_{\text{Calcite}}}$ ) and brucite ( $S_{\text{I}_{\text{Brucite}}}$ ), and the internal partial pressure of  $\text{CO}_2$  ( $P_{\text{CO}_2}$  in atm) as well as for hydrogeochemical modelling. The main focus of modelling was given to  $\text{CO}_2$  exchange between solution and atmosphere, mixing of solutions and precipitation of calcite.

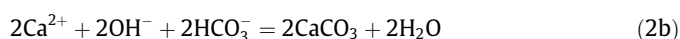
Mineralogical analyses of the precipitates were carried out by X-ray Diffraction (XRD) using a PANalytical X'Pert Pro series diffractometer equipped with a Co-target tube. Chemical digestion of selected precipitates was carried out using 10 wt.% ultrapure double distilled  $\text{HNO}_3$  to check the chemical composition in comparison to the mineralogical content. Chemical analysis of acid digestions was done by ICP-OES (Perkin Elmer 4300) with an analytical precision of  $\pm 5\%$ . Distribution of stable C and O isotopes of the  $\text{CaCO}_3$  precipitates was determined using a fully automated peripheral continuous-flow gas preparation device (Gasbench II), which was connected to a Finnigan DELTA<sup>plus</sup> XP Mass Spectrometer (Dietzel et al., 2009). Respective  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values are given in ‰ relative to VPDB (Vienna Pee Dee Belemnite).

## 3. Mechanisms of $\text{CaCO}_3$ formation

The formation of  $\text{CaCO}_3$  in tunnel drainage systems can be induced by groundwater, which is enriched in  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  at a relatively high internal partial pressure of  $\text{CO}_2$  ( $P_{\text{CO}_2} > 10^{-3.45}$  atm; value of the Earth's atmosphere). The degassing of  $\text{CO}_2$  from the corresponding drainage solution into the atmosphere leads to an increase of pH. Elevated pH shifts the DIC species from  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$ . Accordingly, the degree of saturation with respect to  $\text{CaCO}_3$  increases and precipitation occurs according to the overall reaction

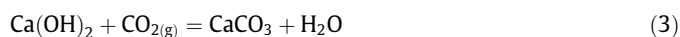


Such scaling or sinter formation can be seen as an analogy to e.g. travertine or speleothem formation in natural environment. On the other hand groundwater can dissolve soluble compounds like portlandite ( $\text{Ca}(\text{OH})_2$ ) as well as Na and K hydroxides by reaction with the shotcrete/concrete of tunnel construction before entering the drainage system. For instance portlandite dissolution results in an increase of  $\text{Ca}^{2+}$  and of pH (up to  $\approx 13$ ), which, by analogy to  $\text{CO}_2$  degassing, shifts DIC species from  $\text{HCO}_3^-$  to  $\text{CO}_3^{2-}$ . Accordingly precipitation of  $\text{CaCO}_3$  according to the reactions



can occur within the matrix of the shotcrete/concrete, in the drainage system or in the receiving stream. For both overall reactions (1) and (2) the  $\text{CO}_3^{2-}$  ion for the formation of  $\text{CaCO}_3$  is generated from the groundwater and, therefore, corresponds to the uptake of soil  $\text{CO}_2$  during infiltration of meteoric solutions and subsequent dissolution of carbonate minerals (e.g. calcite, dolomite) in the aquifer.

Calcium carbonate scaling in highly alkaline environments can also be induced by the absorption of atmospheric  $\text{CO}_2$ . In this case, sinter formation is based on the absorption of atmospheric  $\text{CO}_2$ , subsequent transformation to  $\text{CO}_3^{2-}$  and its precipitation as  $\text{CaCO}_3$  according to the reactions



## 4. Composition of scalings and solutions

### 4.1. Scaling

The X-ray pattern of analysed scalings shows that calcite is the main component in all three tunnels with minor amounts of detrital quartz and silicates such as mica and feldspar. No additional  $\text{CaCO}_3$  polymorphs such as aragonite and vaterite were found. In one sample from WW brucite ( $\text{Mg}(\text{OH})_2$ ) was detected as a minor component. The average chemical composition of the precipitates from chemical analyses of acid digestions is:  $89.8 \pm 4.8$  wt.%  $\text{CaCO}_3$ ,  $1.6 \pm 0.9$  wt.%  $\text{MgCO}_3$ ,  $0.22 \pm 0.03$  wt.%  $\text{SrCO}_3$  and  $0.03 \pm 0.01$  wt.%  $\text{BaCO}_3$ . Remaining solids after acid digestion consist of quartz

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