



$^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ Signatures of Calcite Sinter in Alkaline Drainage Solutions – Proxy for Precipitation Mechanisms

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Drainage systems of tunnels are often a target of scale sintering. In general, such sinter material mainly consists of calcite. Calcite sinter in drainage systems may induce serious problems due to the reduction of cross sections of drainage tubes and the pollution of receiving streams by suspended calcite and ongoing sinter formation.

The aim of the present study is to decipher the mechanisms and kinetics of calcite sinter formation by analyzing the chemical and isotopic composition, $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios, of the drainage solutions and precipitated calcite. Fundamental knowledge about the dynamics and element cycles within such systems are required to develop suitable retaliatory action.

In general, the precipitates consist of about 90 to 95 wt.% calcite with minor amounts of magnesium as well as traces of silica, iron, and aluminium (e.g. detritical silicates like clay minerals, and quartz). The drainage solutions typically exhibit elevated pH values vs. those of the groundwater. The pH can even reach values between 12.3 and 13.2. Such high alkaline drainage solutions are generated from groundwater by strong interaction with the shotcrete of the tunnel construction, whereas less slightly alkaline solutions are due to rather reduced solid-liquid interaction or mixtures of various solutions. Reaction mechanisms at the shotcrete can be followed by high alkaline drainage solution vs. groundwater composition. E.g. depletion of dissolved magnesium and sulfate indicates the formation of ettringite (or thaumasite and gypsum) and brucite ($\text{Mg}(\text{OH})_2$). However, the formation of the alkaline environments is mostly

related to the dissolution of portlandite ($\text{Ca}(\text{OH})_2$) from concrete.

In general, calcite-sinter is related to the dissolved inorganic carbon of ground waters. Nevertheless, great quantities of sinter may also occur in tunnels where ground waters are low in dissolved carbonate (e.g. in areas dominated by sandstone or shale). Moreover, precipitation of calcite continues also in those ground waters generated in carbonate rich areas, although the primary dissolved carbonate is already lost. This may suggest an influence of atmospheric CO_2 . Gaseous carbon dioxide is absorbed into the solution and thus contributes to further precipitation of calcite.

The results show that both mechanisms, precipitation of carbonate from ground water and absorption of atmospheric CO_2 , may be deciphered by the stable isotopic composition of carbon and oxygen in the precipitated calcite. In general, solid CaCO_3 obtained by atmospheric CO_2 -absorption has a $\delta^{13}\text{C}$ -value of about -25 ‰ (PDB), whereas precipitation of CaCO_3 from ground water carbonate implies the characteristic isotopic signature $\delta^{13}\text{C} \approx -13 \text{ ‰}$ (PDB).

The fixation of atmospheric $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in the precipitated calcite is accompanied with a kinetic fractionation. Diffusion and hydroxylation of $^{13}\text{CO}_2$ is slower vs. $^{12}\text{CO}_2$. In this situation, the isotopic composition of the calcite-sinter is obtained by equation

$$\delta^{13}\text{C}_{\text{CaCO}_3(2)} + 10^3 = \alpha \cdot \beta^{0.5} \cdot (\delta^{13}\text{C}_{\text{CO}_2(\text{atm})} + 10^3) \quad (1)$$

, where α and β denote the equilibrium fractionation coefficient between dissolved and solid carbonate ($\alpha = 1.0011$) and the kinetic fractionation coefficient via diffusion and hydroxylation of CO_2 ($\beta = 0.9614$). Thus, isotopic fractionation between precipitated calcite and gaseous CO_2 is $(\alpha \cdot \beta^{0.5} - 1) \cdot 10^3 = -18.4 \text{ ‰}$. Considering $\delta^{13}\text{C}_{\text{CO}_2(\text{atm})} = -7 \text{ ‰}$ of the atmosphere an isotopic composition of calcite-sinter of about -25.4 ‰ is obtained.

For $\delta^{13}\text{C}$ -values higher than -25 ‰ CO_2 -absorption may be superimposed by dissolved bicarbonate derived from ground waters. Values down to -29 ‰ are related to CO_2 -absorption from a mixture of atmospheric CO_2 and CO_2 from combustion of fossil fuel with "light" isotopic values. For example, calcite-sinter with $\delta^{13}\text{C} \approx -29 \text{ ‰}$ implies gaseous CO_2 of about -11 ‰ .

In general, solid CaCO_3 obtained by atmospheric CO_2 -absorption has a $\delta^{13}\text{C}$ - and $\delta^{18}\text{O}$ -value of about -25 and -20 ‰ (PDB), respectively, whereas precipitation of CaCO_3 from groundwater carbonate implies a characteristic isotopic signature $\delta^{13}\text{C} \approx -13 \text{ ‰}$ and $\delta^{18}\text{O} \approx -5 \text{ ‰}$ (PDB). The type and relative amount can be evaluated by the stable isotopic composition of carbon and oxygen in the precipitated calcite.