

Carbonates in mineral clay liners: A risk for long-term security of waste disposal sites? Experimental, geochemical, and isotopic constraints

H. Taubald
M. Satir

University of Tübingen, Department of Geochemistry,
Wilhelmstr. 56, D-72074 Tübingen, Germany

Introduction

Waste disposal sites and contaminated areas comprise aggressive as well as toxic leachates and gas-phases that are able to pollute the hydrosphere, biosphere and atmosphere. In modern geotechnical engineering artificial barrier systems are constructed to protect the environment. They must a) have a very low permeability to avoid mechanical transport of contaminated fluids through the barrier into soil and groundwater and b) have a high capacity to immobilize and adsorb pollutants like heavy metals and organic compounds. Mineral clay liners are commonly accepted and used for this purpose. During the first phase of biological decomposition of organic material in a landfill (aerobic decomposition) acid leachates are produced. Old, abandoned, contaminated sites may also contain highly concentrated acids in batteries, etc. These acids can easily dissolve carbonate phases. This changes the chemical composition of the liner and thus may also change its permeability. The official recommendation in Germany therefore limits the amount of carbonate to max. 15%. Since fundamental knowledge about carbonate dissolution in mineral clay liners is lacking, we have investigated the influence of acid leachates on carbonate-bearing clays, to study the complex interactions expected.

Methods

Since it is difficult to see these processes 'in nature', we tried to simulate natural conditions in the lab in the most realistic way possible. Special permeability cells were constructed (Taubald, *et al.*, 1994), that provide low and variable hydraulic gradients (0 to 5), an open system for gases produced by chemical reactions (gases may escape) and permeation from top to bottom. In order to do a comparative investigation we used two clays with different mineralogical and chemical composition: 1) carbonate-rich clay, c. 35% carbonate, Tertiary age, 'Obere

Süßwassermolasse', Southern Bavaria, 2) carbonate poor clay, c. 3% carbonate, Jurassic age, 'Opalinuston', Southern Baden-Württemberg.

Out of these materials we formed cylindrical samples (12 × 10 cm) and put them, compacted to high density, into the permeability cells. To simulate waste leachates of different chemical composition we treated the samples with one organic and one inorganic acid: a) acetic acid 10%, (pH 2.3), b) a mixture (1:1:1) of concentrated HCl, H₂SO₄, HNO₃, (pH < 0.5). The samples were treated at room temperature (c. 20°C), removed after 15 weeks and cut into 5–8 horizontal slices. Each slice was investigated for carbonate content, to calculate the amount of carbonate dissolved. Additionally the ¹³C- and ¹⁸O-isotope composition of these remaining phases was measured, to constrain dissolution-precipitation processes. C- and O-isotope measurements were performed according to McCrae (1950), the carbonate content of the sample was measured volumetrically as the amount of CO₂ liberated during reaction with phosphoric acid for isotope analysis. Leachates were sampled weekly and pH-values measured.

Results

There is an obvious difference between carbonate-rich and carbonate-poor material. In the first case (c. 35% carbonate) the influence of acid can be traced to a depth of 4–6 cm, where carbonate dissolution occurred. In carbonate-poor (c. 3% carbonate) material, under the same conditions, carbonate dissolution was observed throughout the core. In carbonate-rich material a 'reaction-front' can be observed along which the acid (pH < 2.3) was neutralized to a more harmless fluid (pH 5–7). In carbonate-poor material, due to the low carbonate content, this neutralization could not be performed. The acid migrated through the whole sample with low pH-value. There is clear evidence for this feature by the pH-values of the leachates. Leachates from carbonate-rich material fall in the region between pH 5 and

pH 7, while leachates of carbonate-poor material show lower values and show a decreasing trend with time. This agrees well with data from Cherry (1984), who postulated an 'acid-front retardation factor' in carbonate bearing sandstones due to dissolution of calcite and dolomite caused by acidic leachates from uranium mining activities.

Dissolution of carbonate phases produces H_2CO_3 , HCO_3^- , CO_3^{2-} ions and CO_2 which form a chemical equilibrium, depending on pH-value. These phases show C- and O-isotope fractionation, which means that they have different isotopic signatures under equilibrium conditions. A combined dissolution-precipitation process of carbonate phases changes the isotopic signature of a secondary carbonate phase (Salomons and Mook, 1986; Usdowski *et al.*, 1979). Our data show, that the residual phases in the uppermost sample-slice in carbonate-rich material reveal strongly depleted $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (-40% PDB) compared to primary values (-2 to -6% PDB) for both acids and both clays. The simple model of carbonate dissolution under equilibrium conditions with liberation of CO_2 at 25°C and $\text{pH} < 6$ is able to produce changes of around 10% , with the escaping CO_2 being enriched in the heavy isotope ^{18}O and depleted in ^{13}C and therefore can not explain the observed isotopic changes. We therefore suggest a combined carbonate dissolution-precipitation process and a possible influence of other C- and O-bearing phases, like clay minerals or organic compounds with low $\delta^{13}\text{C}$ values of around -30% PDB.

Conclusions and summary

The break-through point of an acid front in carbonate-poor material depends only on the permeability of the clay. In carbonate-rich material we can postulate a carbonate acid retardation factor, which depends on the amount of carbonate present and the acid capacity of the leachate. However this assumption is only true if we have a relatively homogeneous, fine grained distribution of the carbonates. Carbonatic veins or

joints filled with calcite behave differently and can cause severe problems. But this does not apply for mineral clay liners in waste disposals, since this material is handled mechanically, homogenized and compacted before use. C- and O-isotopic composition of residual and/or newly formed carbonates demonstrate that not only dissolution but also (re-) precipitation of carbonate phases must have occurred, which again has a positive influence, since it may decrease porosity and thus permeability of the clay. Neutralization of acid, aggressive leachates from waste disposals by dissolution of carbonates in mineral clay layers provides two important advantages: 1) leachate shows less aggressivity to other minerals, like clay minerals, that help to achieve low permeability, 2) solubility and mobility of heavy metal decrease with increasing pH. So we conclude that geochemically carbonates do not seem risky but can provide long-term security. Calculations show, that a waste disposal can hardly provide enough acid, to dissolve all carbonate phases present in carbonate-rich material. However, from a geotechnical point of view more research is necessary, since dissolution of carbonates results in a loss of mass, which can cause mechanical problems for engineers.

References

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