

Origin of calcium isotope fractionation in river waters: Evidence from the Strengbach catchment, France

B. CENKI-TOK*, F. CHABAUX, D. LEMARCHAND, P. STILLE, M.-L. BAGARD AND M.-C. PIERRET

Centre de Géochimie de la Surface, UMR 7517, Ecole et Observatoire des Sciences de la Terre 1, rue Blessig, 67084 Strasbourg Cedex, France

*Present address: Universität Bern, Institut für Geologie, Baltzerstrasse 1+3, 3012 Bern, Switzerland (cenkitok@geo.unibe.ch)

Understanding calcium isotope systematics in river and surface waters plays a key role in unravelling the calcium oceanic cycle as well as characterizing chemical weathering processes in continental systems. However, only few studies have focussed on deciphering the factors controlling calcium isotope fractionation in continental river waters. In order to shed light on the origin of calcium fractionation in river waters, we investigated the different reservoirs for calcium isotopes and their interactions in a forested first order scale catchment (Strengbach, France).

Variations of $\delta^{44/40}\text{Ca}$ within springs, brooks and river waters are small (0.17-0.87‰) and display typical values for continental rivers, reflecting the control of lithology on calcium isotopic composition of water on a global scale. Compared to these values, soil solutions are significantly depleted in light calcium ($\delta^{44/40}\text{Ca}$: 1.00 to 1.47‰) whereas vegetation is enriched in light calcium ($\delta^{44/40}\text{Ca}$: -0.98 to +0.19‰). At the small watershed scale, our results suggest that vegetation controls the calcium isotopic composition of waters: (i) the origin of depletion in light calcium in soil solutions is directly linked to calcium recycling and fractionation within plants, (ii) the calcium isotopic composition of the water at the outlet of the watershed shows a yearly cycling directly related to the activity of vegetation.

In summary, surface waters are influenced by vegetation whereas deep waters preserve the calcium isotopic signature inherited from the parent rock. Therefore, calcium isotope analysis clearly helps to evaluate the role of vegetation and to unravel the hydrologic cycle at the watershed scale.

Durability and degradation of oil well cement exposed to a source of H₂S and CO₂ gases

J. CENTENO¹, A. RAMÍREZ², A. BLANCO¹ AND A BALZA¹

¹PDVSA Intevep, Los Teques, Venezuela.

(centenojs@pdvsa.com; blancoa@pdvsa.com;

balzaau@pdvsa.com)

²Instituto de Ciencias de la Tierra, UCV, Venezuela.

(aramire@ciens.ucv.ve)

Introduction

Usually, the oil industry gives relevance to failures in metallic structures produced by the corrosion caused by H₂S and CO₂ and its implication in the well life. The search of new reservoirs in deep environment conditions, in which concentrations of H₂S and CO₂ are noteworthy, requires the study of the sour gas effect on nonmetallic structures, such as oil well cement.

Methods

Recent studies have demonstrated the effect of degradation in the chemical and mechanical properties of oil well cement exposed, in the short term, to aggressive atmospheres, thus, endangering the well life (Centeno *et al.*, 2005). This study shows the influence of H₂S and CO₂ gases and their mixtures, in different H₂S/CO₂ ratios (0.1; 0.2 and 0.4), on the chemical and mechanical properties of cement samples (class G and H) exposed to high pressure and temperature in well bore real conditions, using a exposure time of 20, 40 and 80 days. Test tubes were exposed to the action of a mixture of CO₂/H₂S, dissolved in water, in a Parr reactor for HPHT. The test solution was analyzed by Inductive Coupled Plasma -ICP- (elements) and Ionic Chromatography (anions). Solid phase mineralogy was determinate by SEM and X-ray analysis.

Results and Conclusions

The H₂S and CO₂ mixtures have an effect on cementing material causing a mass profit corresponding to CaCO₃ formation, that is maximum when the H₂S/CO₂ relation approaches to 0.2. This CaCO₃ mass profit was detected with test tube weight comparison, before and after acid attack, and mineralogy analysis. For H₂S/CO₂ ratios > 0.2 a mass loss was observed, which causes degradation of cementing material verified by compressive strength decrease.

The results allow to model the effect of oil well cement dissolution with time, for H₂S/CO₂ ratios < 0.2 using second degree polynomials, in which the dependent variable is a chemical species such as: Ca⁺², Na⁺, K⁺ or SO₄⁻, or a physical measure such as the compressive strength.

References

- Centeno J., Ramirez A., Colina A. y Blanco A. (2005) Dissolution of oil well cement in presence of CO₂/H₂S under HTHP. *Geochimica et Cosmochimica Acta* **69**, supplement 1, pp. 1-915