

Mineralogical and geochemical characteristics and genesis of the sepiolite deposits at Polatlı Basin (Ankara, Turkey)

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The Polatlı basin located north of Ankara, contains sepiolite-rich marly and clayey fluvial and lacustrine sediments that formed during the Late Miocene to Early Pliocene. The mineralogic composition of these sepiolite-rich deposits consists of sepiolite, dolomite and calcite, and palygorskite, quartz, moganite, amorphous silica (opal-CT) and feldspar in subordinate quantities. Sepiolite and dolomite+sepiolite are found in the bottom and calcite+sepiolite in the intermediary level, while calcite+dolomite and calcite (limestone) occur in the upper horizons. Argillaceous layers were generally observed under the limestone layers. Amorphous silica is observed above the dolomite-sepiolite layers as beds and within the sepiolite layers as nodules. The sepiolite, dolostone and limestone succession overlay saponite/aluminum-rich saponitic claystones. Amorphous silica containing sepiolite shows some of the characteristic reflections of sepiolite, but the basal reflection becomes somewhat broader and less intense. Major (Al, Ti, Fe, Mn, K, Na) RE, LIL, HFS and TRT elements are almost exclusively included in saponite and Al-rich saponite, while Mg, Ca, and partly Si are concentrated in the neoformed minerals in the basin. The results of this study demonstrate that the REE and some of HFS, LIL and TRT element patterns are similar. RE, TRT, LIL and partly HFS element content of the carbonate minerals (calcite and dolomite) and sepiolite are similar to each other, while RE and LIL contents are higher in saponite. RE elements show strongly positive correlation to Al₂O₃, Fe₂O₃, TiO₂, Zr and HFS elements and a moderately negative correlation to MgO. PAAS-normalized REE patterns are typically subparallel and show clear depletion. All sample groups have a positive Eu* anomaly, except saponite (0.80). Limestone, dolostone and amorphous silica show a slightly negative Ce* anomaly, while sepiolite and saponite have a slightly positive anomaly.

SEM-EDS applications in mineralogical phases study of oil well cements attacked with H₂S/CO₂ mixtures

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Ordinary Portland cement (OPC) is the main component in cementitious materials used in oil wells construction. The mineralogical changes caused by chemical interactions between this material and acid gases (H₂S and CO₂), has been studied [1, 2]. The behavior of some mineralogical species, that constitute the main OPC phases, can indicate the integrity of this material in terms of compressive strength. Particularly, Ca (OH)₂ transformation in CaCO₃ caused by carbonation process. This study shows the influence of gas mixtures, at different pH₂S/pCO₂ ratios, on the chemical, mineralogical and mechanical properties of cement samples (class G and H) exposed to high pressure (total pressure = 1500 psi) and temperature (160 °C) in well bore real conditions, based on the exposure time (t = 20, 40 and 80 days). In-closed system conditions (Parr reactor type), partial pressure of pCO₂ = 38 atm, and pH₂S = 4, 8 and 16 atm, for 0.1, 0.2 and 0.4 pH₂S/pCO₂ ratio, were used in this work. Mineralogical phases composition was determined by X-Ray diffraction, and scanning electron microscope and energy dispersive spectrometer (SEM-EDS). These techniques can be used to track resulting changes in the cementitious material microstructure (i.e. porosity) as intensity of carbonation, and estimates can be made of possible effects that these changes may have on the performance of the cementitious material. Compressive strength measurements were made after controlled time exposures. The results indicate important changes in mineralogy. The most important H₂S effect is test tube leaching. CaCO₃ formation (vaterite, aragonite and calcite) is the principal effect of CO₂. Both processes affect cementitious materials integrity. For pH₂S/pCO₂ ratios around 0.2, the maximum value of compressive strength is reached. In conclusion, an important relationship between the compressive strength and the pH₂S/pCO₂ quotient was determined, therefore, the integrity of cementitious materials can be estimated according to previous parameters.

[1] Centeno *et al.* (2005) *GCA* **69**, 10. [2] Centeno (2007) Doctoral Lecture UCV, Caracas, Venezuela.