

2.2.P03**Induced structural and compositional modifications on glauconite from dissolution experiments**

A. SANTOS¹, S. FERNANDEZ-BASTERO², T. GARCIA²
AND L. GAGO-DUPORT²

¹Dept. Cristalografía, University of Cadiz, Spain.

²Dept. Geociencias Marinas, University of Vigo, Spain.

The structural modifications and kinetics of glauconite dissolution in acid solutions were examined by performing flow-through experiments over a wide range of pH, from 2 to 7. The aim of this work was to determine the non-stoichiometric dissolution kinetics for the several cations in the glauconite formula (K, Fe, Al, Mg) and to relate these to the induced structural transformations at several stages of the kinetics process. Analyzed glauconite samples were from continental shelf of NW Spain.

HCl-glauconite leaching solutions were prepared at room temperature and aged for times ranging from several hours to one month. In order to determine whether surface chemical composition and structure are modified as a result of the experiments, both the final products and unreacted samples were characterized by following identical procedure.

Characterization of the structural variations of the glauconites following HCl treatment was carried out by XRD following the Rietveld method. Local disorder induced by dissolution was analyzed through radial distribution function (RDF) using reverse Monte Carlo methods. In addition, induced modifications on crystal morphology, porosity, and chemical stoichiometry were characterized by SEM, EDS, BET, and XPS respectively. Comparison of the elemental composition at the surface of both, HCl-treated and untreated glauconite samples show substantial differences after several hours.

Analytical results indicate that the samples treated with acid exhibit a progressive decrease in K, Mg, Fe and Al, indicating that the remaining structural framework is only formed by amorphous silica. Comparison of the XRD pattern for unreacted glauconite with spectra obtained after reaction indicates an increase of the amorphous silica content and a progressive loss of the original mineral structure. Further the RDF analysis show an appreciable variation in the atomic-pairs distribution that can be related to both, the removal of the octahedral cations and pH.

This study has been supported by BTE 2000-0877 CICYT Spanish project.

2.2.P04**Dissolution rate of mercury oxide**

A. J. HOCSMAN^{1,3}, S. DI NEZIO², M. J. AVENA²,
C. P. DE PAULI¹ AND L. CHARLET³

¹INFIQC, Dpto. Físicoquímica, Fac. Ciencias Químicas, Universidad Nacional de Córdoba. 5000, Córdoba, Argentina (ana.hocsman@obs.ujf-grenoble.fr; depauli@fcq.unc.edu.ar)

²Departamento de Química, Universidad Nacional del Sur Av. Alem 1253, 8000 Bahía Blanca, Argentina (sdinezio@criba.edu.ar; mavena@uns.edu.ar)

³LGIT-OSUG, University of Grenoble-I, BP 51, 38041 Grenoble, France (charlet@ujf-grenoble.fr)

Elementary mercury is introduced in the environment as a result of mining and chlorine alkali manufacturing. Since Hg⁰ is slightly soluble, the formation of soluble Hg(II) species from liquid Hg⁰ can be visualized as composed by two main processes. The first one is the oxidation of Hg⁰ droplets to HgO with the formation of a HgO layer, the second one is the dissolution in aqueous media of the oxide and production of soluble Hg(II) species. Each of these processes depends on both thermodynamic and kinetic parameters, which need to be evaluated in order to know what step is controlling the rate of contamination. Therefore such kinetic data are important in predicting the fate and transport of mercury in natural systems.

Dissolution thermodynamics and kinetics of red mercury oxide (HgO) in aqueous media were investigated by a Flow Injection Analysis (FIA) with sequential spectrophotometric detection.

Solubility of red HgO was studied in 0.01M KNO₃ solutions in the pH range 2.2-10.5. A series of experiments were also performed at constant pH (3.5) and various temperatures (4°C-49°C) in order to evaluate the effects of temperature on the solubility of HgO. The solubility is constant between pH 4 and 12, and increases abruptly as pH decreases below 4. The solubility of HgO is between 10⁻³ and 10⁻⁴ M.

The dissolution rate of HgO was followed by measuring the increase in Hg(II) concentration in solution as a function of time. Experiments were performed to determine dissolution rates of red HgO at various pH (T=23±1°C), temperature (pH=3.5) and stirring rate conditions (23±1°C and pH=3.5). Dissolution curves indicate a tridimensional contracting process where particles reduce their radius at a constant rate e.g. 0.00135 μm/sec at pH 2.7 and 24°C. It was observed that the dissolution rate is, like solubility, readily affected by pH. The dissolution rate is constant at pH>4 and increases significantly at pH<4. Temperature has a marked effect on the rate, and the rate increases between 5°C and 50 °C, leading to an activation energy of 32.12 kJ/mol.

Concerning the dissolution mechanism two processes are operating in parallel, with the overall rate reflecting contributions from surface reactions and mass transport. Their relative importance will be discussed.