The Prestige oil spill after a decade: Evaluation of remediation strategies and the role of bioremediation.

J.R. GALLEGO[1]*, A.I. PELÁEZ[1], J. SÁNCHEZ[1], M.J. GCÍA- MTNEZ[2], J.E. ORTIZ[2], T. TORRES[2] AND J.F. LLAMAS[2]

[1]Environmental Biotechnology and Geochemistry Group. University of Oviedo. C/Gonzalo Gut. S/N, 33600-Mieres (Asturias), Spain. (*correspondence: jgallego@uniovi.es)
[2]ETSMinas, Universidad Politécnica de Madrid. C/Ríos Rosas, 21-28003 Madrid, Spain.

In 2002, the Atlantic and Cantabrian shorelines of Spain were affected by the Prestige heavy fuel oil spill. Initially the fuel was physically removed in rocky areas by means of hot pressurized water washing and similar procedures, whereas in sandy beaches other machinery was used. However, bioremediation was also considered given that the destructive effects of the hot pressurized water on the biota, the difficulties to collect oily waste, and other questions related with the grain-size of the sediments affected and the strong fuel adhesion in the shore rocks [1, 2, 3].

Our research carried out several studies all along the coasts in which natural attenuation, biostimulation and bioaugmentation techniques were tested in pilot and full-scale experiments for remediating oil-coated sands, gravels, pebbles, cobbles and boulders. Microbiological control and normalization by means of non-degradable chemical biomarkers were made to monitor these procedures. To improve bioremediation yields, novel *in situ* fresh-water irrigation and on-site techniques were developed, following similar strategies than those habitually used in soil remediation. The results obtained underscored the utility of these innovative designs to be used as an alternative to the limited effectiveness of the application of oleophilic fertilizers, clearly limited by the recalcitrance and by the reduced bioavailability of resin and asphaltene fractions. As a conclusion, long-term strategies for the bioremediation of other spillages with similar characteristics are suggested.

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Evidence of Fe-oxide clusters in obsidians

L. GALOISY, G. CALAS AND N. MENGUY

Institut de Minéralogie et de Physique des Milieux Condensés (IMPMC), UPMC; Université Paris 7; CNRS; 4, Place Jussieu, 75252 Paris Cedex 05, France. (Laurence.galoisy@impmc.upmc.fr)

Iron has long been known to play an important role in determining the properties of natural magmatic liquids. The determination of the sites occupied by ferrous and ferric cations in natural glasses may provide information on the physico-chemical conditions prevailing at the magmatic stage as well as on the cooling conditions of the magma. We discuss the spectroscopic data obtained on the Fe environment in calc-alkaline rhyolitic glasses (obsidians) from various localities, at the light of transmission electron microscopic observations. Fe^{2+} and Fe^{3+} ions partly occur within the glass structure, as indicated by XANES [1], EPR and optical absorption spectroscopy (OAS). OAS reveals that some Fe^{2+} occurs in a regular octahedral site, an unusual environment in glasses.

The presence of Fe-oxide nano-clusters, suspected from previous EPR spectroscopy data, is confirmed by variable-temperature OAS in all the obsidians investigated. Specific absorption bands, assigned to Fe-Fe and Fe-Ti intervalence charge transfers (IVCT), are characterized by a spectacular intensity enhancement at low temperature (10K). This thermally-activated behavior shows an activation energy similar to that observed for IVCT in various minerals. The evidence of specific Fe^{2+} sites and of IVCT processes, indicate the presence of Fe-oxide clusters. These clusters, showing a local re-arrangement around Fe, are related to the cooling history of the glass, as they are not found in synthetic glasses [2]. They may be also precursors of the amorphous and crystalline Fe-oxides (Ti-magnetite and magnetite), 5-10 nm large, evidenced using TEM. The existence of these clusters and their nature seem to be related to the conditions of formation of the investigated obsidians and they may obscure the information brought by these glasses about its magmatic history.

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