

A new conceptual model for interpreting the redox behavior of magnetite in anoxic environments

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Magnetite (Fe_3O_4) is common in the environment, forming as a result of biotic and abiotic reduction of iron oxides, as well as the oxidation of ferrous iron and iron metal. In studies of reactions between magnetite, aqueous Fe^{II} , and environmental contaminants, several inconsistencies exist in the reported rates and extent of contaminant removal. For example, reported rates of carbon tetrachloride reduction vary over two orders of magnitude [1,2], and the extent of U^{VI} reduction varies from no reduction [3] to nearly complete reduction [4] under similar experimental conditions. The underlying cause for these observed discrepancies remains unclear in the literature.

Here, we revisit the reaction of magnetite with Fe^{II} and nitrobenzene, introducing the initial magnetite Fe^{2+} content as an important variable to be considered when assessing rates of contaminant reduction. Using selective isotope Mössbauer spectroscopy, we re-interpret traditional sorption isotherm and dissolution data, demonstrating that the reaction of Fe^{II} with magnetite involves sorption, electron transfer, and formation of magnetite with an increased Fe^{2+} content. We also argue that surface complexation models do not adequately describe the magnetite- Fe^{II} system, and a more appropriate model is that of a semiconductor which is negatively (n) doped by electron transfer following Fe^{II} uptake. For contaminant reduction, we find that the reactivity between magnetite and nitrobenzene is correlated to the initial magnetite Fe^{2+} content, and may provide an explanation to the existing discrepancies found in the literature regarding rates of contaminant reduction by magnetite

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Trace-elements of the hydrocarbon's reduced systems and the origin of oil and gas

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The study of deep origin of huge Romashkin oil field is based on research of microelement composition of oil and on deep structure of the crystalline basement and of the earth's crust. The study is focused on the basement and sedimentary rocks penetrated by wells on the South Tatarstan Arch and on the oil from Romashkino and other oil fields of Volgo-Ural region.

The first results of the analysis of have shown that levels of many chalcophilic trace elements in oil considerably exceed their levels in sedimentary rocks and in the upper part of the Earth's crust. The oils of Tatarstan are characterized by the presence of palladium and iridium. Studying of isotope structure of oil has shown that oil from various horizons and areas is characterized by different evolution of isotope composition. It has been found that asphaltenes have a distinct, positive europium-produced anomaly and a ratio of Eu/Sm reaching 1.16 that is obviously not characteristic of the upper crust formations.

The segregation of the fluids in the upper portions of the Earth's crust and the formation of bitumens causes the latter to inherit the geochemical composition of the reduced systems. This process is accompanied by the differentiation in the accumulation of various microelements in carbonaceous substances that is governed by temperature, i.e. that depends on the class of the synthesised bitumens and on the properties of organometallic compounds.

Track radiography has detected, in relation to uranium, no secondary epigenetic enrichment of bitumens with metal due to oxygen-containing waters or other solutions. One can see a quite even distribution of heavy metals. The behaviours of carbon, sulphur and phosphorus are similar.

These results confirm the presence of high actinolite and lanthanide contents in bitumens. Thorium is a dominant radioactive element, with the Th/U ratio being higher than 10 and, in some cases, up to 60. Lanthanides are mainly represented by the light ones with cerium accumulations.

Due to the difference in properties of lithophilous and chalcophilous organometallic compounds, the former are likely to be rejected when thermobaric characteristics change, while stable compounds with As, Sb, Hg, Se and other elements are more likely to remain in the fluid and its derivatives, to accumulate in relatively light fractions and to be concentrated in asphalts. Analysis of the distribution of radioactive elements in carbonaceous compounds of various compositions has indicated that the organouranium complexes in reduced systems are more stable than the thorium ones.