Soft x-ray scanning transmission spectromicroscopy of cementitious materials

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Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of hazardous and radioactive wastes in underground repositories. Cement is used to condition the waste materials and to construct the engineered barrier systems. Therefore, a mechanistic understanding of the processes governing the binding of heavy metals in cement systems is essential for long-term predictions of the environmental impact of cement-stabilized waste forms. From a chemical standpoint, cement is a very heterogeneous material with discrete particles in the nano to micrometer size range, which makes it an ideal system to be investigated with scanning transmission x-ray microscopy (STXM).

In this study the soft x-ray STXM end station at the Advanced Light Source-Molecular Environmental Science (ALS-MES) Beamline 11.0.2 has been utilized to investigate metal precipitates formed in Ni- and Co-doped cement pastes. The ALS-MES STXM collects both images and near-edge x-ray absorption fine structure (NEXAFS) spectra with a spatial resolution of 30 nm. NEXAFS spectra of the Ni and Co $2p_{3/2}$ edges were utilized to collect spectroscopic information on the Ni- and Co-precipitates formed in the cement matrix. This study complements previous micro-spectroscopic investigations on the speciation of Ni(II) and Co(II) in cement pastes (Vespa *et al*., 2006, 2007). For Ni(II)-doped cement pastes, the formation of a Ni(II)-Al layered double hydroxide phase was observed by Vespa *et al*. (2006). In Co(II)-doped cement pastes, however, partial oxidation of the initially added Co(II), and the formation of CoOOH, $Co(OH)_2$ and Co-phyllosilicate phases were observed (Vespa *et al*. 2007). Since only mixtures of Co(II) and Co(III) phases could be detected on the micrometer scale the question remained open whether this observation resulted from the limited spatial resolution of micro-X-ray absorption spectroscopy. The complementary STXM investigations reveal that variations in the speciation of Ni and Co in the cement matrix occur on the nanometer scale. Thus, the study demonstrated that STXM is a powerful tool to gain information on the nanometer scale on the distribution and speciation in systems that are relevant in connection with the safe disposal of cement-stabilized hazardous and radioactive waste.

References

Vespa M. *et al*. (2006), *Environ. Sci. Technol.,* **40**, 7702.

Vespa M. *et al*. (2007), *Environ. Sci. Technol.,* **41**, 1902.

Xingcheng abiogenic alkane gas field in Songliao Basin, China

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Xingcheng gas field is located in the Daqing and Anda city of Heilongjiang province and geologically in the volcanic uplift zone in the centre of Xujiaweizi rift, Songliao basin. Six exploration wells have been drilled in this gas field. The proved geologic reserve of natural gas in Lower Cretaceous volcanic and conglomerate rocks is $459.84\times10^8 m^3$ within an area of 41.70 km^2. Xuxi, Xuzhong and Xudong faults developed in a long period in Xujiaweizi rift. Xuxi and Xuzhong faults extend 58 and 96 kilometers, respectively, and the faults throw is up to 1800m. Faults cut off the basement rock, reach the mantle magma chamber, lead to violate volcanic movements during multiple stages. The main stage of volcano eruption is Yingcheng Formation of Lower Cretaceous.

The natural gas geochemistry characteristics show that:①CH_4 accounts for more than 93%, and the hydrocarbon gases above C_2 account for ~3%. The $\delta^{13}C_1$ values which range from -25.9‰ to -28.9‰ are the heaviest among the alkane gases, and the trend of $\delta^{13}C$ values gets lighter with increasing carbon numbers ($\delta^{13}C_1>\delta^{13}C_2>\delta^{13}C_3>\delta^{13}C_4$). So the gases of Xingcheng gas field is abiogenic (Dai *et al*., 2005).②The $\delta^{13}C$ values of volcanic-magmatic and mantle genetic carbon dioxide are -6±2‰ (Dai *et al*., 2005) .The $\delta^{13}C_{CO2}$ values of Xingcheng gas field are within the range of -4.8‰~-8.2‰, so the CO_2 is of magma-mantle genetic characteristic ; ③The values of $^3He/^4He$ in the upper mantle are between 1.1×10^{-5} and 1.4×10^{-5}, and the values of $^3He/^4He$ in radiogenic strata are from 10^{-7} to 10^{-9} (Wang , 1989) . The value of $^3He/^4He$ in the gas field is 10^{-6}, which may be the results of ^3He from the mantle. It also proves that some of the alkane gases originate from the mantle ; ④ Many experiments show that catarinite can catalysize the reaction between CO_2 and H_2 to form CH_4 in hydrothermal fluid (Horita J *et al*.,1999), and chromites can catalysize the reaction to form CH_4, C_2H_6 and C_3H_8 (Foustoukos D I *et al*.,2004). In Xingcheng gas field, CO_2 exists widely and H_2 is discovered in some wells. The active stage of volcano and hydrothermal fluid movements are multiple. At present, the average temperature gradient in Songliao basin is 3.7℃/100m and the maximum reaches 6.1℃/100m. All the conditions are favorable for the reaction of Fischer-Tropsch synthesis to form abiogenic alkane gas.

References

Dai, J. X. *et al*., 2005. Organic Geochemistry 36(12), 1664-1688

Foustoukos, D. I. *et al*., 2004. Science 304(5673), 1002-1005

Horita, J. *et al*., 1999. Science 285(5430), 1055-1057

Wang, X. B., 1989. Noble gas isotope geochemistry and cosmochemistry. Beijing: Science Press (in Chinese)