第 29 卷 增刊 高 能 物 理 与 核 物 理 Vol. 29, Supp.
2005 年 12 月 HIGH ENERGY PHYSICS AND NUCLEAR PHYSICS Dec., 2005

XANES Study of Hg Sorption Products on Montmorillonite at High Temperatures*

CHU Wang-Sheng[1,2] WU Zi-Yu[1,2;1)] LIU Wen-Han[1] D. Malferrari[3]
M. F. Brigatti[3] G. Cibin[4] A. Marcelli[4]

1 (Deparment of Physics, University of Science and Technology of China, Hefei 230026, China)
2 (Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, CAS, Beijing 100049, China)
3 (Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, L.go S. Eufemia 19, Italy)
4 (INFN-Laboratori Nazionali di Frascati, P.O.Box 13, 00044 Frascati, Italy)

Abstract The Hg L_3-edge XANES spectra of montmorillonite treated with $Hg(NO_3)_2$ 0.01M aqueous solution and the mixing solution of $Hg(NO_3)_2$ 0.01M aqueous solution and cysteine 0.01M aqueous solution have been measured at several high temperatures. The adsorption and desorption of mercury in Hg-rich montmorillonite minerals and the effect of cysteine on the adsorption of mercury by this clay mineral were studied. Our analysis shows that mercury is six fold coordinated by water molecules and the oxygen atoms of montmorillonite surface without the amino acid introduction. Mercury atoms prefer to bond with sulphur atoms of the amino acid cysteine to form more stable Hg-S bonds when the amino acid cysteine has been introduced. This result suggests that the treatment with the amino acid enhances the stability of mercury sorbed by the montmorillonite mineral and efficiently retard the release of mercury ions into the geosphere.

Key words mercury, montmorillonite, XANES

1 Introduction

Mercury is one of the most important contaminants in water and sediment because of its high volatility. Even if present in traces, its high toxicity makes it an environmental threat in industrial, mining, and domestic wastes[1]. It is well known that the toxic properties of any element are critically dependant by the molecular form; for example, dialkylmercury derivatives are toxic even at low levels, whereas mercuric selenide has a relatively low toxicity[2]. Therefore, by binding the heavy metals with its coordination of nonmetallic elements, the toxicity of the heavy metals can be removed.

Fine-particle materials that present a large surface area such as oxides, oxyhydroxides and layer silicates are among the principal sorbents of the metal species[3]. Furthermore, clay minerals are ubiquitous components of natural environments and control many environmental processes. Clays structure can be assimilated to polymers, species formed by molecular units repeated in modular way. Clays belong to the class of phyllosilicate minerals, which are made of sheets of silica tetrahedra, bound to octahedrally coordinated divalent or trivalent metal cations. The tetrahedral and octahedral sheets are bound into layers that form a repeated modular structure. The interlayer space can be filled by water, mobile mono- and divalent ions like K or Ca, and solvated ions. This layered structure, characterized by weak electrostatic bonds in the interlayer space, gives clays a great ability to sorb most chemical species. Thus, sorption,

---

*Supported by National Natural Science Funds for Distinguished Young Scholar (10125523) and National Natural Science Foundation of China (10490190, 10490194)

1) E-mail: wuzy@mail.ihep.ac.cn

diffusion and precipitation reactions at the mineral-water interface can significantly modify the release of absorbed metal ions into the environment[4].

The knowledge of the heavy metal binding to the mineral structure is of fundamental importance to predict mobility and long term behavior of heavy metals in natural systems. Several manuscripts devoted to the investigations of pollution of different clay minerals with heavy metals (i.e. Cu, Cd and Hg) and amino acids (i.e. cysteine and glycine) have been recently published[5—7]. In these studies the local environment of metals has been characterized by X-ray absorption spectroscopy (XAS) trying to clarify the binding mechanisms of metals and their subsequent mobilization. The results demonstrated that Cu and Cd are six fold coordinated by water molecules in the interlayer, whereas Hg is tetrahedrally coordinated by water molecules and forms phases such as montroydite (HgO). Studies on clay mineral treated also with amino acids (cysteine and glycine) indicated a short range order in which Cu preferentially bonds to the aminic and carbossilic group of the amino acids cysteine. While the results obtained for Cu and Cd are satisfactory and allow to describe the relationship between clay minerals, heavy metals and organic-metallic complexes, the problem is still open for Hg and Hg-amino acid polluted clays. Preliminary XAS results point out the presence of two different populations of Hg cations - Hg tetrahedrally coordinated by water molecules and mercury oxide, but are not able to explain the thermal events, providing evidence for the release of Hg cation at high temperature.

In order to gain better insight into the relationship between the structure, the composition of sorbed phases and the mercury desorption in clay minerals, that are very important not only to prevent the possible evolution of polluted environments but also to set up technologies capable to recover or to make inert pollutant phases, we measured Hg L_3-edge XANES spectra of montmorillonite treated with two Hg-contained solutions: $Hg(NO_3)_2$ 0.01M aqueous solution and the mixing solution of $Hg(NO_3)_2$ 0.01M aqueous solution and cysteine 0.01M aqueous solution at different high temperatures.

2 Materials and method

Montmorillonite minerals used in our samples was from Gonzales County, Texas, USA. Details of the mineralogical, chemical and surface properties of montmorillonite can be found in Ref. [8]. The Hg(Ⅱ) 0.01M stock aqueous solution used for all treatments was obtained from the dissolution of $Hg(NO_3)_2 \cdot 7H_2O$ analytical grade reagent and acidified with nitric acid until pH 2.0 to avoid Hg precipitation. Cysteine 0.01M solution was prepared using a 99% pure from Carlo Erba reagent. Hg-rich montmorillonites were prepared by mixing approximately 10 g of each montmorillonite sample with 250mL of Hg(Ⅱ) 0.01M solution. The suspensions were stirred overnight at room temperature, and then centrifuged; the solution was then aspirated off and fresh solution was added; the sequence was repeated three times. Excess salts were removed from the homoionic clays by dialysis until the aspirated solution tested negative with $AgNO_3$. Finally, filtrates from all ion-exchange experiments were analyzed by atomic absorption spectrophotometry, to check the presence of metal cations used in the exchange.

XANES spectra at the Hg L_3 edge were measured using the Si (111) double crystal monochromator at the X-Ray absorption station (beam line 1W1B) of the Beijing Synchrotron Radiation Facility (BSRF). We measured the two model compounds in transmission mode using ionization chambers, while fluorescence yield detection was used for the samples investigated: $Hg(NO_3)_2$ 0.01M aqueous solution and the mixing solution of $Hg(NO_3)_2$ 0.01M aqueous solution and cysteine 0.01M aqueous solution, labeled by MHg and MHgCys respectively, at several temperatures. The storage ring was working at the typical energy of 2.2GeV with a current decreasing from $\sim$120mA to $\sim$60mA during a typical run of 12 hours.

3 Results and discussion

Fig. 1 shows the Hg L_3-edge XANES spectra of the two model compounds HgS and HgO. XANES spectra of HgS and HgO compounds show similar features, labeled as A, B, C and D, because of the similar chemical environment around the absorbing atoms in these two systems. Indeed, while HgS and HgO compound structure belongs to different space groups the absorbing mercury atoms are in both systems coordinated by six atoms as the first nearest neighbor shell. HgS belongs to the space group P3221 whereas Hg(OH)$_2$ belongs to Imm2. In both cases, the six next-neighbour atoms form a distorted octahedron. According to previous investigations on a similar compound[9], the features A, B, C and D has to be assigned to the 2p core state transition to $5d_z^2$, $5d_{x^2-y^2}$, $5d_{xy}$ and $5d_{xz}+5d_{yz}$ states, respectively. Because mercury is present in Hg^{2+} oxidation state both in HgO and HgS, the peak A is located at the same energy position for the two XANES spectra of these compounds. However, the position of peaks B, C and D of the XANES spectrum of HgO is shifted to high energy if compared to HgS, reflecting the lengthening of the Hg-S bond respect to the Hg-O bond length.

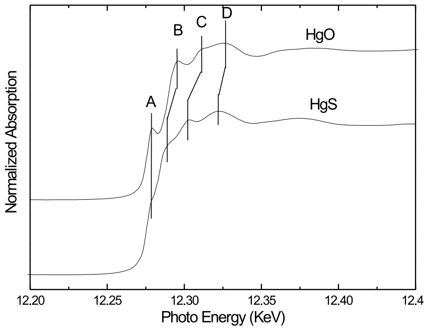

Fig. 1. Normalized Hg L_3-edge XANES spectra of the two model compounds HgS and HgO. The XANES features were labeled as A, B, C and D.

Fig. 2 and 3 show the Hg L_3-edge XANES spectra of the two Hg-rich montmorillonite minerals vs. temperature, and insets in both figures show the normalized XANES spectra. Following the position of the peak A in these samples mercury is Hg^{2+} in both the two Hg-rich montmorillonite minerals. Peak A and B in the XANES spectrum of the MHg sample at room temperature are located at about 12.281 and 12.296 keV respectively, the same as in the HgO model compound. Actually, the nearest neighbor chemical environment of mercury atoms in the MHg sample is similar to HgO, e.g., Hg is coordinated by six oxygen atoms in the first shell. However, the XANES spectrum of the MHg sample does not shows C and D features clearly, but just present a broad peak labeled E addressing large distortion effects of the first shell around the mercury atom in the MHg.

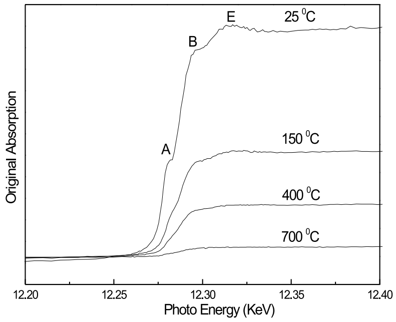

Fig. 2. Original Hg L_3-edge XANES spectra of a montmorillonite mineral treated with Hg-contained solution at 25℃, 150℃, 400℃ and 700℃. The inset shows the corresponding normalized XANES.

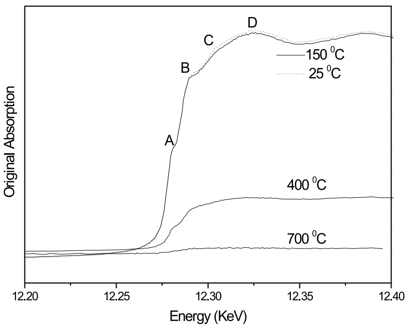

Fig. 3. Original Hg L_3-edge XANES spectra of montmorillonite mineral treated with Hg-Cysteine solution at 25℃, 150℃, 400℃ and 700℃. The inset shows the corresponding normalized XANES.

The XANES spectrum of the MHgCys sample at room temperature, that is the montmorillonite mineral treated with the mixing solution of Hg(NO$_3$)$_2$ 0.01M aqueous solution and cysteine 0.01M aqueous solution, presents four main features also labeled as A, B, C and D. These peaks are located at 12.281, 12.290, 12.304 and 12.324keV respectively, the same as in the HgS model compound. This suggests the presence of mercury coordinated by six sulphur atoms, forming Hg-S bonds. Because the feature B at 12.296keV in the XANES spectrum of HgO, used as the fingerprint[10, 11] of Hg-O bonding, is overimposed to the broad peak C, data at romm temperature does not allow to determine if Hg-O bonding exists in the MHgCys sample.

In order to determine the local chemical environment of sorbed mercury atoms, stability and desorption process, Hg L_3-edge XANES spectra were performed vs. temperature within a sample cell inside an oven working up to 900℃. For MHg, the absorption intensity decreases with the temperature. But the peak A do not disappear up to 400℃. Data suggest that not only Hg-H_2O complex, but also other more stable Hg-O bonds are formed in the montmorillonite mineral treated with the Hg-contained solution.

The desorption process shows a two step behavior. At first, the bond between mercury and water molecules gradually breaks up and some mercury is released. Later, bonds between mercury and oxygen atoms of the montmorillonite surface gradually decompose. When the temperature is increased up to 700℃, the emission of mercury continues up to the almost complete desorption of Hg in this sample.

Looking now at the MHgCys behaviour, the XANES spectrum does not show significant variations at temperature lower than 150℃, indicating that Hg-S bonds between Hg and cysteine are formed before Hg-H_2O complex. Thus, due to the presence of the cysteine amino acid, the Hg-H_2O complex concentration in the MHgCys is lower then in MHg. When the temperature increases up to 400℃, the absorption intensity decreases but peak A does not disappear up to 700℃. As a consequence Hg-O bonds between mercury and oxygen atoms of the montmorillonite surface are formed and, the Hg-S bonds are stable at temperatures lower than 400℃. The desorption process can be also divided into two steps. The first in which Hg-O bonds between mercury and oxygen atoms of the montmorillonite surface gradually breaks up and mercury is partially released. In the second one the Hg-S bonds between mercury and cysteine gradually decompose.

4　Summary

Temperature controlled Hg L_3-edge XANES spectra of two montmorillonite minerals treated with Hg-contained solution and Hg-Cysteine solution respectively have been collected and analysed. By comparison with XANES spectra of model compounds we address that:

a) mercury is present as Hg^{2+} in both Hg-rich montmorillonite minerals;

b) in the montmorillonite treated with Hg-containing solutions, mercury can be adsorbed by formation of Hg-H_2O complex and the Hg-O bonds between Hg and the oxygen atoms of the montmorillonite surface. All mercury atoms are six fold coordinated by water molecules or oxygen atoms;

c) the amino acid may enhance the adsorption effect of the mineral clay and prevent mercury by decomposition and desorption, through the formation of more stable Hg-S bonds. However, in the mineral clay Hg-S bonds begin to decompose at high temperature. The result suggests that treatments with amino acids may enhance the stability of mercury sorbed by montmorillonite minerals and retard efficiently the release of mercury ions into the geosphere.

References

1 Hudson R J M et al. Water Air Soil Pollution, 1995, **80**: 265

2 Wagemann R et al. Sci. Total Environ., 1998, **218**: 19

3 Collins C R, Sherman D M, Ragnardottir K V. Journal of Colloid and Interface Science, 1999, **219**: 345

4 Gagnon C et al. Marine Chemistry, 1997, **59**: 158

5 Benincasa E et al. Clay Minerals, 2000, **35**: 645

6 Benincasa E et al. Applied Clay Science, 2002, **21**: 191

7 Cardelli A et al. Phys. Chem. Miner, 2003, **30**: 54

8 Olphen H van, Fripiat J J. Data Handbook for Clay Materials and other Non-metallic Minerals, 1979, Pergamon Press, Oxford, 343

9 WU Zi-Yu, Saini N L, Bianconi A. Phys. Rev., 2001, **B64**: 092507

10 WU Zi-Yu et al. Phys. Rev., 1997, **B55**: 2570

11 WU Zi-Yu et al. Phys. Rev., 1999, **B60**: 9216

利用 X 射线近边吸收谱学方法研究蒙脱石在高温下吸附汞金属的行为*

储旺盛[1,2] 吴自玉[1,2;1)] 刘文汉[1] D. Malferrari[3]
M. F. Brigatti[3] G. Cibin[4] A. Marcelli[4]

1 (中国科学技术大学物理学系 合肥 230026)
2 (中国科学院高能物理研究所北京同步辐射实验室 北京 100049)
3 (Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, L.go S. Eufemia 19, Italy)
4 (INFN-Laboratori Nazionali di Frascati, P.O.Box 13, 00044 Frascati, Italy)

摘要 测量了分别用汞水溶液、汞和半胱氨酸混合溶液处理的蒙脱石样品在高温下汞 L_3 边X射线近边吸收谱. 利用这个方法研究了汞金属在蒙脱石中的吸附和解吸附行为以及氨基酸对吸附汞吸附行为的影响. 研究结果显示在没有氨基酸介入的情况下, 蒙脱石中吸附的汞被 6 个水分子配位, 或者被蒙脱石表面的氧原子配位; 当引入半胱氨酸时, 汞优先于氨基酸中的硫原子配位, 形成更稳定的 Hg-S 键. 这个结果说明氨基酸的引入能够使得蒙脱石更稳定的吸附汞金属离子, 大大缓解汞离子向生物圈中迁移.

关键词 汞 蒙脱石 X射线近边吸收谱

---

*国家杰出青年科学基金(10125523)和国家自然科学基金(10490190, 10490194)资助

1) E-mail: wuzy@mail.ihep.ac.cn