

Chemical Speciation of Chromium in Drilling Muds

Takeyoshi Taguchi *, Mitsuru Yoshii † and Kohzo Shinoda ‡

*X-ray Research Laboratory, RIGAKU Corporation, 3-9-12 Matsubara-cho, Akishima-shi, Tokyo 196-8666, Japan

†Mud Technical Center, Telnite Co.,Ltd., 1-2-14 Ohama, Sakata-shi, Yamagata 998-0064, Japan

‡The Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai-shi, Miyagi 980-8577, Japan

Abstract. Drilling muds are made of bentonite and other clays, and/or polymers, mixed with water to the desired viscosity. Without the drilling muds, corporations could not drill for oil and gas and we would have hardly any of the fuels and lubricants considered essential for modern industrial civilization. There are hundreds of drilling muds used and some kinds of drilling muds contain chromium. The chemical states of chromium in muds have been studied carefully due to concerns about the environmental influence. However it is difficult to determine the chemical state of chromium in drilling muds directly by conventional analytical methods. We have studied the chemical form of chromium in drilling muds by using a laboratory XAFS system and a synchrotron facility.

Keywords: Drilling Muds, Chromium, XANES

PACS: 07.88.+y

INTRODUCTION

Drilling muds are made of bentonite and other clays, and/or polymers, mixed with water to the desired viscosity. The drilling muds do the following essential jobs in oil and gas wells:

- Lubricate the drill bit, bearings, mud pump and drill pipe, particularly as it wears against the sides of the well when drilling deviated wells around corners
- Provide hydraulic pressure to the motor that drives the drill bit at the bottom of the hole
- Clean and cool the drill bit as it cuts into the rock
- Provide information to the drillers about what is happening downhole - by monitoring the behavior, flow-rate, pressure and composition of the drilling fluid
- Prevent well blowouts - by including very heavy minerals such as barites to counteract the pressure in the hole.

As described above, drilling muds play an important role in drilling. Without them, corporations could not drill for oil and gas and we would have hardly any of the fuels and lubricants considered essential for modern industrial civilization.

There are hundreds of drilling muds used and some kinds of drilling muds contain chromium and its chemical states have been studied due to concerns about the environmental influence. Chromium (Cr) is the seventh most abundant element on earth [1]. It

occurs in several oxidation states ranging from Cr^{2-} to Cr^{6+} , with the trivalent and hexavalent states being the most stable and common in terrestrial environments. Chromium can be both beneficial and toxic to animals and humans depending on its oxidation state and concentration. At low concentration, Cr^{3+} is essential for animal and human health. Unlike Cr^{3+} , Cr^{6+} is a potent, extremely toxic carcinogen and may cause death to animals and humans if ingested in large doses. Therefore it is extremely important to know the chemical forms of chromium in drilling muds.

SPECIMEN

Some drilling muds with trade names "Tellig", "Lignate" and "BM-nite" contain chromium from 1.4 to 4.6wt%. Figure 1 shows the main part of the manufacturing process of "Lignate" (Telnite Co.). Sodium dichromate turns to sodium chromate under alkaline environment (Fig. 1.1). The sodium chromate reacts with lignosulphates and produces "Lignate" (Fig. 1.2). X-ray diffraction data was measured with a RIGAKU Ultima-III diffractometer and the diffraction pattern did not match that of known chromium compounds. This means that all the sodium dichromate and sodium chromate was used in the reaction and no source to produce Cr(VI) ion was left. The final chemical form of the reaction is not confirmed since single crystals have not been obtained

so far. It is often difficult to produce single crystals from this type of chemicals. Thus, the exact crystal structure is not determined, but the assumed structure is supported by several analytical results. Chromium contained in "Lignate" is supposed to form a complex with lignosulphates. Such complexes are called chelate compounds and are very stable and with usually a very low toxicity. The electrical potential of drilling fluids was measured and compared with that of chromic ion solutions. The electrical potential of drilling fluid is on the reduction side, the opposite of chromic ions that are on the oxidation side. Hence drilling muds cannot oxidize an object and it are not toxic. Furthermore, Cr(VI) oxidizes coexisting material and it is reduced and turned to Cr(III). As the drilling fluids contain a lot of organic materials that can be oxidized easily and with high temperatures in far depths providing a reductive environment due to the lack of oxygen, Cr(VI) is thought to be reduced quickly even if it exists. Hence there is small probability that Cr(VI) exists in drilling fluids [2].

Even though drilling muds are proved harmless, whether the chemical form is Cr(VI) or Cr(III) has been argued.

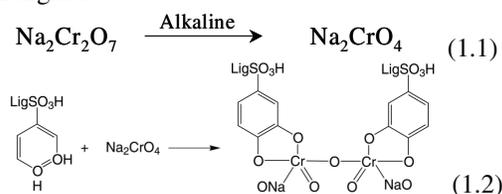


FIGURE 1. Assumed manufacturing process of drilling muds "Lignate".

CHROMIUM SPECIATION

Conventional Methods

JIS (Japanese Industrial Standards) describes the method to identify chromium species as following:

When trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}) coexist in the water, adding aqueous ammonia changes trivalent chromium to a chromium hydroxide. The chromium hydroxide dissolves to the water and is precipitated. After filtration, hexavalent chromium remains in the solution and the quantity is determined by absorptiometry with diphenylcarbazide or atomic absorption spectrochemical analysis. If a chromium complex coexists with trivalent chromium and hexavalent chromium, the chromium complex does not react with ammonium and is detected as chromium metal by the atomic absorption spectrochemical analysis. The chromium complex is not quantified by the absorptiometry with diphenylcarbazide, but it affects the quantitative

accuracy of hexavalent chromium. If the chromium complex is colored, the absorptiometry cannot be used for the quantitative analysis. The JIS regulation defines that the hexavalent chromium cannot be quantified if the hexavalent chromium and a chromium complex coexist [3]. As chelate compounds do not react with ammonia, they do not produce any deposit. Moreover the sample liquid is black. Therefore Cr(VI) in "Lignate", if it exists, cannot be quantified by the method defined by JIS regulation.

X-ray Absorption Spectroscopy

XANES spectra have been used to specify the chemical species of chromium in materials [4-7]. The typical XANES spectra of Cr(III): Cr_2O_3 and Cr(VI): $\text{K}_2\text{Cr}_2\text{O}_7$ are shown in Fig. 2. The most obvious difference between Cr(III) and Cr(VI) XANES spectra is the intensity of the pre-edge peak. The theory of these K-absorption edge transitions has been clearly discussed and modeled [8]. In the centrosymmetric, octahedral symmetry of Cr(III) compounds, the $1s$ to $3d$ transition is dipole forbidden. Hence the pre-edge peak of Cr(III) is small and indistinct. In the tetrahedral coordination of Cr(VI) in the chromate anion, i.e. a non-centrosymmetric environment, orbitals from the oxygen ligands mix with the Cr $3d$ orbitals to produce empty anti-bonding orbitals for which an intense dipole transition is allowed. This is evident in the large pre-edge peak for Cr(VI) in the chromate anion. Therefore the intensity of this pre-edge peak has been used as an index to identify chromium species.

EXPERIMENTAL AND RESULTS

Three drilling muds samples were prepared for XAFS experiments. Sample 1 is "Lignate" as prepared and it is in powder form. Sample 2 is drilling muds containing "Lignate" and prepared under the same condition as for use at a drilling site. Sample 3 is the same as Sample 2 but "aged", or boiled at 150°C for one hour, in order to reproduce the used state. Both Samples 2 and 3 are liquefied. Chromium K-edge XANES and EXAFS of those three samples were measured together with Cr_2O_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ powder as standard materials.

The same samples were examined both using a laboratory XAFS system (RIGAKU R-EXXAFS Super) and at the synchrotron radiation facility (Ritsumeikan University, SR center, BL-4) on different occasions. Figure 2 shows the data taken at the Ritsumeikan University SR center. The data taken on the laboratory system was identical. The only difference was the data acquisition time. The

synchrotron took 3 hours for one spectrum and the laboratory system took one day per spectrum. As drilling muds sample contain water, the water absorbed large amounts of the 6-keV X-ray photons. Therefore the transmission mode was not applicable. Moreover the chromium amount contained in Samples 2 and 3 is about 14 mg/L and the amount is too little for transmission experiment. Hence the data were taken by fluorescence mode using a SSD (solid state detector) for detecting fluorescence signals.

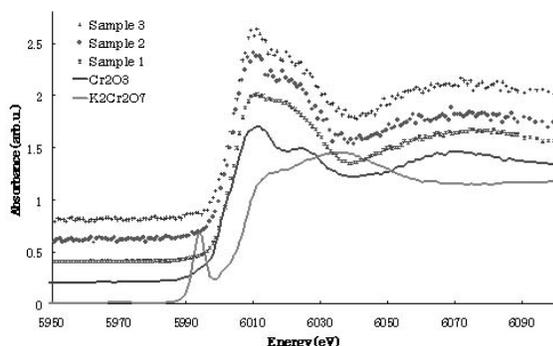


FIGURE 2. Cr K-edge XANES spectra of “Lignite” at different treatment stage, together with Cr_2O_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ as reference materials.

The pre-edge peak of Cr(VI) is not observed for any of the three drilling muds samples. Their XANES spectra show similarity to that of Cr_2O_3 . Therefore octahedral symmetry around chromium atom is suggested for drilling muds. In the XANES spectra of the muds samples, the peak at 6010 eV of Sample 2 and Sample 3 are much sharper than that of Sample 1. This difference may be caused by hydration. The hydration is thought to enhance the symmetry. This hypothesis is supported by EXAFS analysis result described in the next section.

The structural parameters of Cr-O were obtained by ordinary EXAFS analysis procedure using REX2000 [9]. Comparing FOURIER power spectra, the 1st neighbor peak position of the muds samples are close to the position of Cr-O of Cr_2O_3 . Thus we applied empirical backscattering amplitude and phase shift taken from the Cr_2O_3 EXAFS spectrum in the fitting of the EXAFS spectra for the muds samples. The residual errors were around 7 to 8% for all three muds samples. The fitting result is shown in Table 2. The bond length of Sample 1 is shorter than that of Cr_2O_3 and the coordination number larger. This could be explained as follows. There are two chromium-to-oxygen bond lengths in Cr_2O_3 . The tetrahedral 6-fold Cr_2O_3 has three oxygens at 1.962 Å and another three oxygens at 2.009 Å. EXAFS cannot separate this difference. Hence the average distance is obtained. Moreover, as the EXAFS signal is the sum of the

scattered wave from each atom, a small shift in interatomic distance between surrounding atoms reduces the EXAFS oscillation amplitude and this makes the nominal coordination number small. We have simulated two different models. The 2-shell model is assuming three oxygens at 1.962 Å and the other three at 2.009 Å. The 1-shell model is assuming all six oxygen at 1.986 Å, i.e. the average of 1.962 Å and 2.009 Å. The peak height of the 1-shell model is 5% greater than that of the 2-shell model. The larger coordination number of Samples 2 and 3 could be explained by that the hydration enhanced the uniformity of bond length and reduced the dampening effect by thermal vibration.

Based on both XANES and EXAFS analyses, we conclude that chromium in “Lignite” is 6-fold Cr(III). The assumed chemical formula of “Lignite” needs to be modified.

TABLE 2. Structural parameters of Cr-O (N: coordination number, and R: inter-atomic distance)

| | N | R (Å) |
|-----------------------------------|------|-------|
| $\text{K}_2\text{Cr}_2\text{O}_7$ | 4.00 | 1.66 |
| Cr_2O_3 | 6.00 | 1.99 |
| Sample 1 | 6.97 | 1.96 |
| Sample 2 | 7.99 | 1.97 |
| Sample 3 | 8.03 | 1.98 |

CONCLUSION

The chemical state of chromium in drilling muds was studied using X-ray absorption spectroscopy. The result suggests that chromium in “Lignite”, commercially used drilling muds, exists as harmless Cr(III).

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