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Arsenic Removal by Hydroxyapatite-based Ceramics

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The removal of arsenic in geothermal water was carried out by using hydroxyapatite-based materials including the industrial waste, such as bovine bone and hydroxyapatite modified by a solid solution with SiO_2 (SiAp). The existence of arsenic in hydroxyapatite was examined by XANES measurements. The use of these hydroxyapatite-based materials results in a significantly lower environmental loading approach in order to purify arsenic contamination of drinking well waters.

Geothermal power plants for the electricity generation and hot springs use large amounts of geothermal hot water (>373 K) containing high arsenic concentrations (3 to 4 ppm). In fact, large amounts of water with arsenic are throw out as wastewater.[1,2] In Japan, the effluent standard and the environmental quality standard were 0.1 and 0.01 ppm, respectively. In geothermal hot water, As^{3+} mostly exists under geothermal conditions, i.e., high temperature (373 to 573 K) and high pressure (up to ten atms), and is gradually oxidized to As^{5+} with time under ambient temperature and pressure. Usually, a coagulation process with aluminum sulfate (PAC) is used in water clarification treatments, but this process is not effective enough to decrease the arsenic concentration.[3–5] Furthermore, the coprecipitation of arsenic with other metal ions is also attempted but not useful for the large amounts of polluted water. Activated carbons also have a poor ability of effective arsenic removal owing to the low interaction between arsenic and the absorbent.[4] However, hydroxyapatite possesses the ability of ion exchange into its apatite structure. And previously, we have found that hydroxyapatite modified by solid solution with SiO_2 showed the ability of effective removal of various ions, e.g., Cd^{2+}, because of the defect formation, such as anion vacancy, caused by the incorporation of SiO_4^{4-} into PO_4^{3-} site for the compensation of the charge balance.[6,7] In this study, the simultaneous removal of arsenic from geothermal water was successfully achieved by ion exchange using some hydroxyapatites. Furthermore, the presence of arsenic in these hydroxyapatites was examined by XANES measurements.

Table 1 shows the elements of geothermal water in Kakkonda as well as standard supplying water in Japan. In this study, highly pure hydroxyapatite (HAP) spherical powder (1–2 μm in particle size from Taihei Chem.) and bovine bone powder (Eccera Co.) were used. This bovine bone powder was obtained by crashing bovine bone lump after the heat treatment at 1273 K and contained some impurities (Fe, 154 ppm; Mg, 6900 ppm; Na, 7600 ppm; <5 μm in particle size, angular shape).[6] In addition, hydroxyapatites modified by solid solution with spherical SiO_2 (SiAp: <1 μm in particle size) were prepared under hydrothermal conditions for 4 days, as previously reported by authors.[8] Each hydroxyapatite powder (0.1 g) was poured in a stainless bombe with 20 mL of geothermal hot water (approximately 373 K) and subsequently kept at 423 K. After immersion, arsenic concentration was measured with ICP equipment (ICPS-1000, Shimadzu, Kyoto, Japan).

Table 1. Elemental analysis of geothermal water and supplying water in Japan

	Na	Ca	Fe	As	pH
Geothermal water in Kakkonda	696	28.9	<0.01	3.25	8.5
Standard in Japan	<200	<300	<0.3	<0.01	5.8–8.6

Figure 1 shows the time dependence of arsenic concentration in geothermal water for various hydroxyapatites at 423 K under hydrothermal conditions. Pure hydroxyapatite (HAP) and bovine bone powder show the ability of arsenic removal up to 1.8 and 0.8 ppm, respectively. However, in case of SiAp, the concentration of As^{5+} decreased below 0.3 ppm after 17-h immersion under hydrothermal conditions. This high ability of arsenic removal for SiAp is thought to be attributed to defect formation by solid solution of SiO_4^{4-} into PO_4^{3-} sites in the hydroxyapatite structure, as above-mentioned.[6–9] In case of bovine bone, high ability of arsenic uptake was thought to be attributed to the apatite-structure with defects, resulted from both incorporation of carbonate into PO_4^{3-} of apatite and calcium-deficiency.[6–11] These bovine bone and SiAp after 1-h immersion in geothermal water under hydrothermal condition contained higher arsenic concentrations (12.1 ppm for bovine bone and 38.2 ppm for SiAp), compared to 3.6 ppm for pure hydroxyapatite.

After the arsenic uptake from geothermal hot water, each hydroxyapatite was removed, separated from geothermal water,

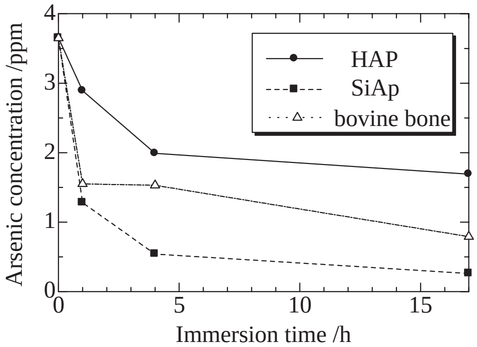

Figure 1. Time dependence of arsenic concentration after immersion in geothermal water for various hydroxyapatites under the hydrothermal condition.

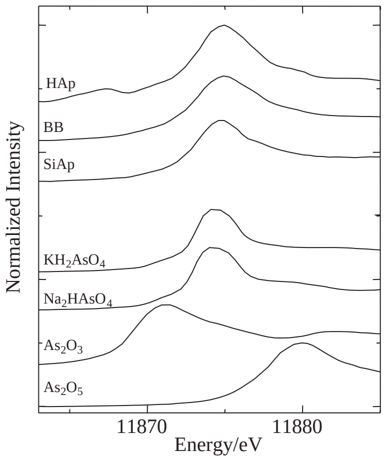

Figure 2. XANES of As K-edge in various hydroxyapatites and reference As compounds. HAP = pure hydroxyapatite, BB = bovine bone, SiAp = hydroxyapatite modified by a solid solution with SiO_2.

and subsequently thoroughly washed with deionized water. The washed samples were dried in the oven at 373 K. XANES was measured for each sample before and after arsenic uptake. Figure 2 shows the results of XANES of As K-edge in some hydroxyapatite, As_2O_3, As_2O_5, KH_2AsO_4, and Na_2HAsO_4 for comparison at SPring 8 (BL01). XANES spectra show that pure hydroxyapatite (HAP), bovine bone (BB) and SiAp containing As^{5+}, that is thought to exist as $H_2AsO_4{}^-$ or $HAsO_4{}^{2-}$ in hydroxyapatite. Consequently these XANES results imply obviously that arsenic for these hydroxyapatites after arsenic uptake stably replaced $PO_4{}^{3-}$ as $H_2AsO_4{}^-$ or $HAsO_4{}^{2-}$ in the apatite structure, not absorption on the surface of hydroxyapatite, because no arsenic was released from samples washed with deionized water after immersion tests according to our results.

The use of some hydroxyapatites with SiO_2 was found effective in the removal of arsenic from geothermal hot water. It is expected that pure hydroxyapatite, SiAp, and bovine bone as a hydroxyapatite source are able to decrease the arsenic concentrations in geothermal water and hot spring waters. Especially, the effective utilization of bovine bone can lead to a recycling of industrial waste related with BSE problems.

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