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STABILIZATION OF METAL-LOADED ION-EXCHANGE RESIN WITH A POROUS SILICA SUPPORTER THROUGH THERMAL TREATMENT

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ABSTRACT

A new ion exchanger with porous silica as a supporting material and diphosphonic acid as a functional chelating group has been developed at ANL for the effective removal of transition metals and actinide ions from very acidic radioactive liquid wastes. The applicability of this resin for the treatment of low- and/or intermediate-level aqueous waste from nuclear power plants (NPP) has not been reported in scientific literature, but is under study now in Korea. The major radioisotopes in NPP radioactive liquid waste are Cs and Co in neutral pH ranges. This study on the thermal stabilization of metal-loaded waste resin has been carried out in parallel with the sorption experiment. Thermal treatment of metal (Co, Cs or U) loaded resin was accomplished to see the possibility of enhancing the safety and stability of the final product during transportation and disposal. In this paper, characteristics of the metal-loaded resins before and after heat treatment at three different thermal conditions were investigated and compared with each other to see the effectiveness of the thermal treatment method.

INTRODUCTION

A new ion exchange resin (hereinafter referred as "DP resin") with porous silica as a supporter and diphosphonic acid ligand as a chelating group has been developed in research collaboration between Argonne National Laboratory (ANL) and the University of Tennessee to remove long-lived actinide and other highly charged metal ions from acidic aqueous solutions while providing radiation resistance superior to ion exchange materials based on organic polymer supporters. Although this resin can strongly sorb highly charged metal ions such as lanthanides and most actinides, the resin itself is a poor waste form candidate due to its organic content which raises concerns about hydrogen gas generation and leakage of sorbed metal ions if high levels of alpha emitting isotopes are sorbed into the resin and left in contact with it (1, 2). The dried resin contains about 20wt% of organic materials and 0.68 mmole of phosphorus per gram of dried resin. One possible procedure of treating metal-loaded resin is to destroy the organic materials through wet oxidation. However, this procedure is time and reagent consuming. The other alternative is heating the metal-loaded resins to remove its organic content and thermally densify it to dense silica at temperatures lower than the normal operating temperature of a conventional vitrification process. It has been shown by other researchers that the originally sorbed actinide or lanthanide ions are nanoencapsulated and chemically fixed as phosphates by thermal densification (3, 4). In these studies, heating DP resin in air oxidized its organic content to water and carbon dioxide and its phosphonate groups to phosphoric acid while leaving sorbed metal ions as phosphates in the pores of the silica. Continued heating caused pore collapse within the silica thereby microencapsulating the chemically fixed metal ions in vitreous silica, which was reported to occur at temperatures as low as 1000^{o}C. Although this resin was proved to be effective in uptaking highly charged metal ions from very acidic solutions, no work at pH value above 2 or with mineral acids, such as phosphoric, that can strongly complex metal ions has been reported. Application of the DP resin to treat low-level radioactive liquid waste from nuclear power plants, whose major radioisotopes are Cs and Co in neutral pH ranges, is now under way (5). Thermal stabilization of metal-loaded resin is being done in parallel with the sorption study mentioned above. In this paper, experimental results on the heat treatment of used resins that contain Cs, Co or U will be presented.

EXPERIMENTAL

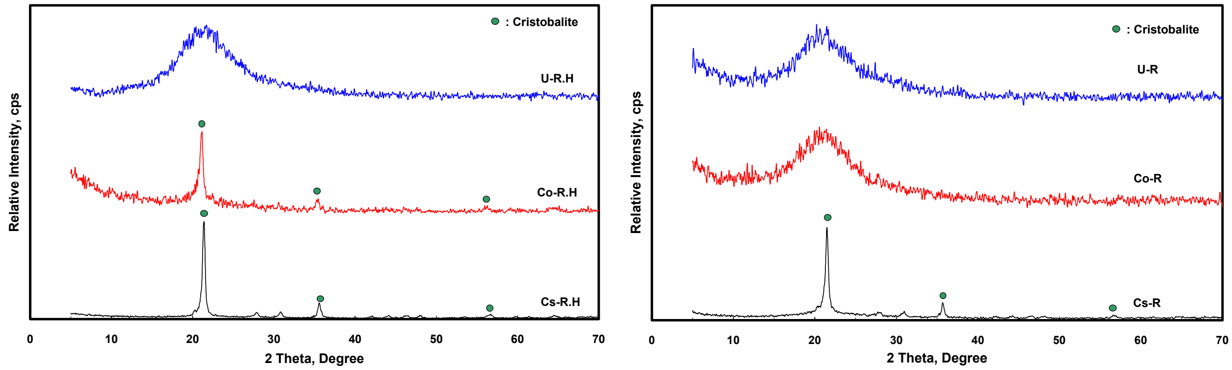
Metal-loaded DP resin (hereinafter referred as "MD resin") was prepared by contacting the virgin DP resin (hereinafter referred as "VD resin") with simulated waste solution containing Cs, Co or U (780, 100, and 100 ppm, respectively) in a batch reactor for 72 hours with a mild agitation. The amount of solution and resin was 1.6L and 50g, respectively, for each batch. The batch ion exchange conditions were set the same as that of a previous sorption study (5). After the batch sorption step, the metal-loaded resins were dried at 105^{o}C for 24 hours and then thermally treated at different heating conditions such as the final target temperature, the heating rate and/or the sample holding time at the target temperature. Based on the experimental results of preliminary heating tests (6), the following three different thermal conditions were chosen for the final heat treatment of MD resins; 1) H : hold the MD resin for 3 hours in a furnace maintained at constant temperature of 1000^{o}C, 2) R : place the MD resin in a furnace at room temperature, raise the furnace temperature to 1000 ^{o}C with a heating rate of 15 ^{o}C /min and then hold the sample at that temperature for one and a half hours, and 3) RH : follow the same procedure as R condition except the sample holding time for 3 hours.

The amount of metal sorbed into the resin was measured through wet chemical analysis by using AA or ICP spectrometer. The dried and heat-treated MD resins were characterized with respect to crystal phase by XRD (Rigaku Co.), change in the microstructure and composition by SEM-EDS (Oxoford Co., Model INFA), particle size distribution by Coulter Counter (Multisizer III), bonding by FT-IR (Nicolet Co., Model 800), and chemical durability by PCT method.

RESULTS AND DISCUSSION

As-received VD resins were fine particles (diameter 150~250μm) white in color and contained moisture. The thermogravimetric analysis (TGA, Seiko Model TG/DTA 6300) of those resins under air atmosphere showed that they were composed of 38.84% water, 11.34% organic materials, and 49.82% inorganic materials. The oxidation of organic materials occurred in the range between about 300°C and 640°C and the exothermic peak in DTA curve supported this result. Preliminary experiments with VD resins has been conducted at various heating conditions to determine the proper heat treatment conditions for MD resins. Analyzing the heat-treated VD resins in terms of pore and particle size reduction, degree of oxidation, and Si/P dissolution resistance showed that densification of porous silica was possible at temperatures below 1000°C and a longer residence time at higher temperatures seemed favorable to the complete oxidation of the organic contents and good corrosion resistance (6). The three thermal treatment conditions (H, R, and RH in the previous section) were chosen based on these preliminary experimental results and applied to treat the MD resins.

XRD patterns of some heat-treated MD resins are shown in Fig. 1. Although not shown in the figure, all the dried MD resins showed amorphous peak patterns like U-loaded MD resins shown in Fig. 1 and the MD resins treated at H condition showed the same peak patterns as those treated at RH condition.

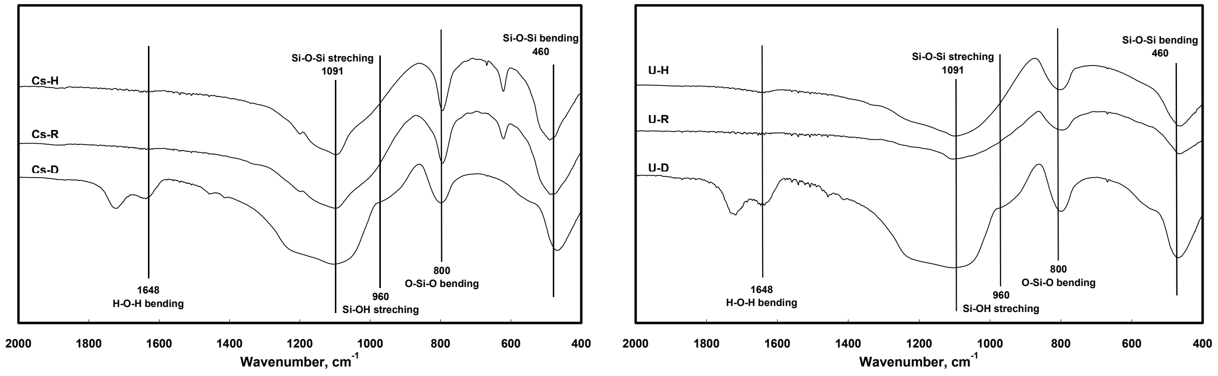


(a) RH condition (15°C/min, 1.5 hour at 1000°C)   (b) R condition (15°C/min, 30 min at 1000°C)

Figure 1. XRD patterns of MD resins after thermal treatment at different heating conditions.

Since the XRD patterns of dried MD resins were very similar to those of dried VD resins, the adsorption of metal ions on the DP resin could not affect the original crystal structure except when external energy (like heating) was applied to change the chemical binding of metal (nuclide)-phosphorous-silica. Under heat treatment condition of R, the Co- or U-loaded MD resins were amorphous, while Cs-loaded resin showed cristobalite peaks. But when enough heat was applied (condition RH and H), the Co-loaded MD resin also showed characteristic cristobalite peaks, while U-loaded MD resins kept its amorphous form. This was thought due to the difference in the bonding strength and supplied energy. The DP resin was found to have different sorption strengths depending on the ion valence. Some doubly charged ions are significantly sorbed and most triply charged ions strongly and nearly irreversibly sorbed (1). In this experiment, the phosphonic acid group on the DP resin had strongly adsorbed the metal ions in the order of uranium, cobalt, and cesium.

As shown in Fig. 2, the FT-IR analysis on the dried and heat-treated MD resins showed the existence of Si-O-Si bending (460cm^{-1}), O-Si-O bending (800cm^{-1}), and Si-O-Si stretching (1091cm^{-1}), which are the characteristic bonds of silica. The Si-OH stretching (960 cm^{-1}) and H-O-H bending (1648cm^{-1}) peaks with hydroxyl group that had been found in dried MD resin disappeared when the resin was thermally treated. The fact that the dried VD resin contained Si-OH bonding in spite of the existence of organic functional groups covering the surface of silica supporter means that resin has additional ion-exchange capacity to remove metal anions. However, the primary purpose of FT-IR analysis, that is detection of the chemical bonds related to the phosphorous element, was not successful. Especially, peak for Si-O-P (1140cm^{-1}) bonding was not found because of the small content of phosphorous and the possibility of peak overlapping with Si-O-Si stretching bond. It is notable that MD resins with cristobalite crystal phase showed characteristic FT-IR peak near 640cm^{-1}, while amorphous MD resins did not show such peak.



(a) Cs-loaded MD resin

(b) U-loaded MD resin

Figure 2. FT-IR spectra for (a) Cs-loaded and (b) U-loaded MD resins before and after heat treatment.

The particle sizes of as-received DP resins were in the range of 40~550μm and average diameter was about 200μm. After drying the resin the average size reduced to around 100μm. This was thought to happen due to the swelling of the organic layer on the as-received DP resin that contained a high content of moisture. The average size of MD resin was further reduced to around 40μm after heat treatment. Porosimetric analysis using the Hg-intrusion method was performed to see the effect of heat treatment on the pore size distribution and density of VD resin. After heat treatment, the fraction of small pores ranging from 0.01 to 0.1μm was greatly reduced and density increased from 1.71 to 2.19g/cm^3. Evidently, the volume reduction of DP resin through thermal treatment could be achieved as a consequence of the destruction of the organic content of DP resin and thermal densification of the porous silica supporter.

SEM analysis showed that the adsorbed metal ions were evenly distributed on the surface of resin even after the heat treatment. This means that the oxidation of the organic materials and functional groups proceeded so gently as not to disturb the homogeneity of metal distribution. The SEM photograph for the U-loaded MD resin treated at RH condition and the result of sectional U mapping are shown in Fig. 3. The SEM image confirmed the size reduction as well. All the Cs- or Co-loaded MD resins at all thermal conditions and U-loaded MD resins at H or R condition showed the same morphology and homogeneous ion distribution pattern as those of U-loaded MD resin at RH condition. The uranium distribution on the small white particles (denoted as W) was uniform and the same as that on the bulk particle (denoted as B). Hence the white phase seemed to be small fragments of MP resin.

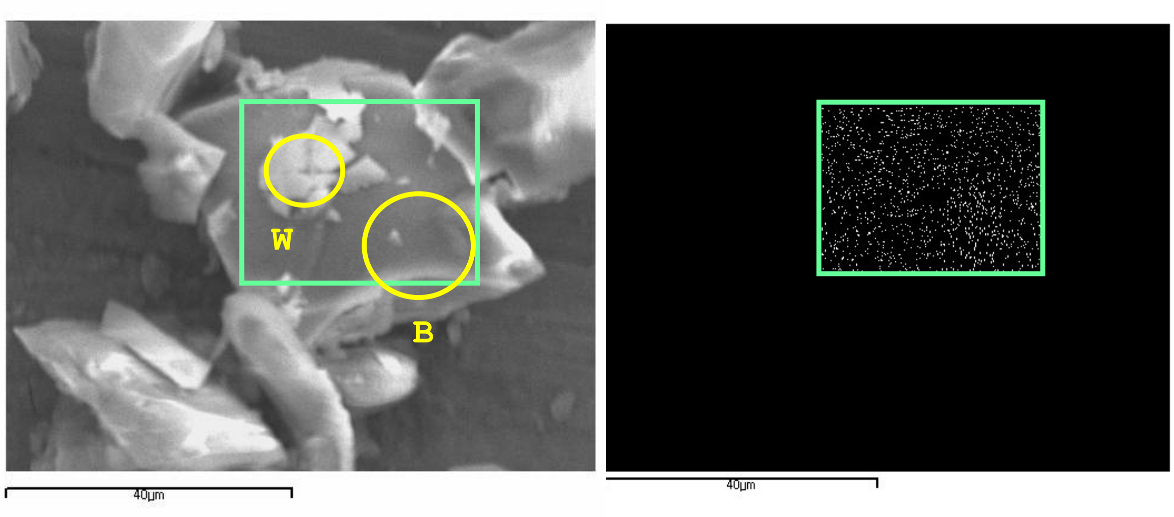


Figure 3. SEM photograph and uranium map of U-loaded MD resin after heat treatment at RH condition.

Compositions of two small sections denoted as W and B in Fig. 3 and that of a broad area of the MD resins (at 40 magnifications) were analyzed by using SEM-EDS and compared with each other. As shown in Table I, the differences in the composition of Si, P, or U were so small that the white phase could be regarded as identical to the main bulk matrix.

Table I. Elemental composition analyzed from the micro-structure of U-loaded MD resin after heat treatment at RH condition.

Phase Component	Overall area	White phase	Black phase
Oxygen	54.08 (-)	55.98 (-)	52.41 (-)
Silicon	45.09 (98.51)	43.38 (98.57)	46.06 (98.52)
Phosphorous	0.32 (0.70)	0.30 (0.68)	0.33 (0.71)
Uranium	0.36 (0.79)	0.33 (0.75)	0.36 (0.77)

The chemical durability was examined through the PCT leaching test (7). The PCT leaching test was conducted at 90°C for 28 days using demineralized distilled water as a leachant solution. Although the standard PCT leaching test should be conducted for 7 or 28 days without changing the leachant solution, we replaced the leachant, in this experiment, in accordance with the interval in the MCC-1P test method (8) in order to investigate the leaching behavior of sorbed metals with leaching time. The amount of leachant and heat-treated MD resin was 40ml and 4g, respectively. Regardless of the metal species, the amount of metal leached sharply increased during the first few days and then decreased to reach nearly the steady state after one week of leaching. The MD resins treated at H or RH condition showed better leach resistance than that treated at R condition. The cumulative amount leached (CAL) of Cs from MD resins treated at H or RH condition was about one half of that from MD resin treated at R condition. The CAL of Co showed similar result to that of Cs with a change of heating condition but the CAL of Co was about two third of Cs after leaching for 28 days. For uranium, however, the CAL of MD resin treated at H condition at 28 days of leaching was about 5 mg/L, which was comparably lower than that from MD resins treated at RH condition (about 25 mg/L) or at R condition (about 45 mg/L). The leach resistance was good in the order of U, Co, and Cs. Consequently, it could be concluded that thermal treatment condition of longer residence time at higher temperature seemed favorable to get the final product with good chemical durability.

CONCLUSIONS

As a part of developing new ion exchange technology with DP resin for the treatment of low- and /or intermediate-level liquid radioactive wastes generated from the nuclear power plants, thermal stabilization of the DP resin that already sorbed simulated radioisotopes was carried out. The metal-loaded DP resins were treated at three different thermal conditions and the products were characterized with respect to crystal phase by XRD, change in the microstructure and composition by SEM-EDS, particle size distribution by Coulter Counter, bonding by FT-IR, and chemical durability by PCT method. Cristobalite crystal phase was found for Cs-loaded resin under all thermal conditions and for Co-loaded resin treated at a higher temperature and for a long holding time, while all the U-loaded resins were amorphous. This is thought to happen due to the difference in binding forces between metal ions and phosphorous ion. The high leaching resistance of uranium ions in the PCT leaching test revealed the high selectivity and thus strong binding force of uranium ions with diphosphonic acid ligands. It was evident that volume reduction and destruction of organic components of the metal-loaded resins would be possible through thermal treatment only. However, the final product maintained its original powder form that requires very high temperature and/or additional flux materials to convert it into a monolithic waste form due to the high melting temperature of the base-material, silica.

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