Gas Chromatography Separation of H_2-D_2-Ar Using Pd/K

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Abstract. A new type of gas chromatographic technique was developed using Pd/Kieselgur as functional materials. It could separate H_2-D_2-Ar mixtures near room temperature with simply operation procedure without introducing any other replacement gas. This method was investigated using 63g Pd/K with two cascaded columns. The palladium content of the Pd/K was about 38.1±0.1wt% with the particle sizes of 200~350 micrometer. The H-D separation was tested at different operation conditions including the columns temperatures, the feeding gases flux and hydrogen isotopes content. The average separation factor was 13.5 under the conditions of 273 K in the columns, 10SCCM as the feeding gas flux, and 2.6at% of hydrogen isotopes in the mixed gas. Deuterium content in outflow of the first column reached 89.01at% from 37.5at% in feed gas. The results show that the separation of protium-deuterium would be better when the protium and deuterium content in raw gas within 6at%, with a gas flux of 10SCCM and a lower temperature. The new chromatographic separation has a potential for separation and recovery of hydrogen isotope out of the tritium extraction systems in breeding Test Blanket Modules.

Keywords: Hydrogen isotope; separation; Chromatography; Pd/K

1. Introduction

Hydrogen isotope separation is the very important technology of deuterium and tritium nuclear fuel circle in fusion reactor. Many methods have been developed to separation hydrogen isotopes, such as cryogenic distillation [1,2], gas chromatography[3,4], thermal cycling absorption press[5,6]. These methods can meet the request of fusion reactor running, but these techniques aren’t very consummate. For example, the cryogenic distillation would run at cryogenic temperature 20~25 K depending on the isotopic fraction, and this technique have some disadvantages, such as complex configuration, high running cost, large tritium holdup in system.

Palladium has the best hydrogen isotope effect so far, so the palladium is selected as the hydrogen isotopes separation materials in gas chromatography to separate the hydrogen isotopes. Gas chromatography as a technique separation hydrogen isotope has been already studied and reported by other investigators. K. Watanabe[7,8] and their research group had do much work to separate hydrogen isotopes using gas chromatography with Pd-Pt. In this work, a new kind of gas chromatographic technique was developed to separate H_2-D_2-Ar mixtures by use of Pd/Kieselgur. The effluent gases out of the tritium extraction systems in breeding Test Blanket Modules (TBMs) are mostly tritium-deuterium-helium mixtures. Because of the tritium radioactivity, the hydrogen isotopes T_2-D_2 were displaced by H_2-D_2 in this work. The basic process of this method as follows: when H_2-D_2-Ar mixtures pass through a Pd-column, H_2 is absorbed by Pd firstly, and then D_2 is absorbed and displaced gradually by H_2 in mixtures. The different distribution of H_2、D_2 content is formed later in lengthways of column. When the absorption of protium is saturated, the outflow from column is pure D_2 and can be collected. When protium is detected from outflow, the gases in column will be pure H_2. In this way, separation of H_2、D_2 is achieved.

2. Experiments

2.1. Materials

Gases used were the mixtures of Ar, H_2 and D_2. Their purities were guaranteed as 99.99%, 99.9% and 99.7%, respectively.

Pd/Kieselgur manufactured by Northwest University of China was used as functional materials packed in separation columns. The palladium content of Pd/K whose particle sizes were 200~350 micrometer was about 38.1±0.1wt %. The specific surface area of Pd/K was 0.7575m^2/g by BET method using Kr at liquid nitrogen 77K in AUTOSORB-1. Fig. 1 shows the surface appearance and the primary component of Pd/K powders analyzed by scanning electron microscope. The light part in fig.1 was the kieselgur. The surface of kieselgur and Pd was rough and had many anomalous holes which were propitious to the reaction of materials with hydrogen isotopes and the exchange of hydrogen isotopes.

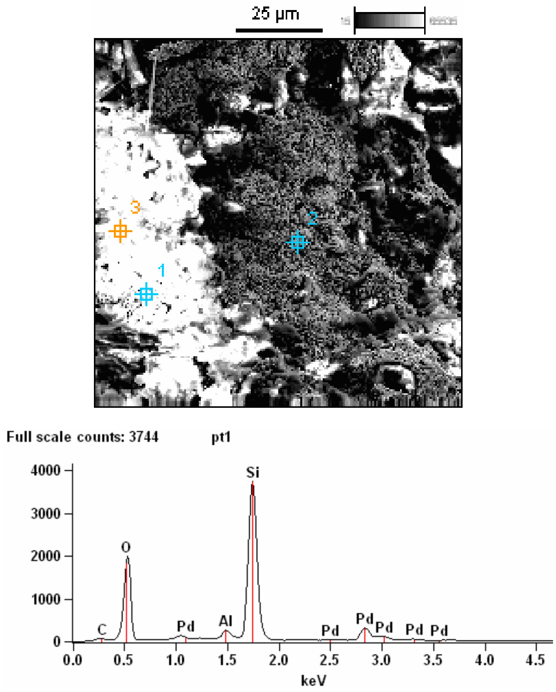

FIG.1. The SEM image and EDS of Pd/K

2.2. Apparatus

The gas chromatographic system mainly consisted of two separation columns, a raw gas reservoir, columns cooling and heating equipment and so on. They were connected to each other with stainless steel tubes. The two columns connected in series packed with about 63g Pd/K were made of copper tube of 0.6cm in diameter and 250cm、270cm in length. The columns were combined with a quadrupole mass spectrometer from In Process Instruments with the model number of GAM 400. To measure the content of hydrogen isotope, a part of the effluent gas from the end of each column was introduced into the quadrupole mass spectrometer through a valve and analyzed with the mass spectrometer

2.3. Procedures

The Pd/K packed in the columns was preheated at 523K in a flow of H_2 gas at a flux of 15SCCM for 2h to remove adsorbed impurities on the surface. Subsequently, the columns were cooled to a given operation temperature. During this procedure, the raw gas mixtures of Ar, H_2 and D_2 passed through the two columns in a given operation temperature and flux, the effluent gas was introduced into the mass spectrometer after about 4~5 min. The two columns were sampled in turn at a 2 min interval, namely, the effluent gas of the first column was firstly introduced into the mass spectrometer, and then the effluent gas of the second column was introduced into the mass spectrometer after 2 min. The pressure of raw gas was controlled at about 0.3MPa and the pressure of the system was kept at about 0.1MPa during the experiment.

The separation factor of protium and deuterium in the column as follows:

$$q_{H,D} = \frac{(c_H / c_D)_{inlet}}{(c_H / c_D)_{outlet}} \qquad (1)$$

c_H and c_D were stand for the mol percentage of protium and deuterium, respectively.

3. Results and Discussion

3.1. Temperature Dependence

Fig.3 shows the temperature dependence of the separation for the raw gas mixture with 1.63%H_2-0.97%D_2-97.4%Ar, where the flux was 10SCCM and the temperatures were 273K、298K、313K，respectively. The ordinate shows the mol percentage of the protium and deuterium in the effluent gas, as determined with the mass spectrometer. The abscissa gives the collection counts after injection the raw gas into the columns.

It was observed that deuterium eluted from the column faster than protium and the hydrogen isotopes eluted from column 1 faster than column 2. The hydrogen isotopes eluted from column 1 after 150 min and they didn’t elute from column 2 in 250 min at 273K. The hydrogen isotopes eluted from two columns after 84 min, 170 min at 298K, respectively and the hydrogen isotopes eluted from two columns after 60 min, 140 min at 313K, respectively. This figure also indicated that the affection on separation of temperature was remarkably, when the column temperature was higher, the hydrogen isotopes can elute from the columns faster.

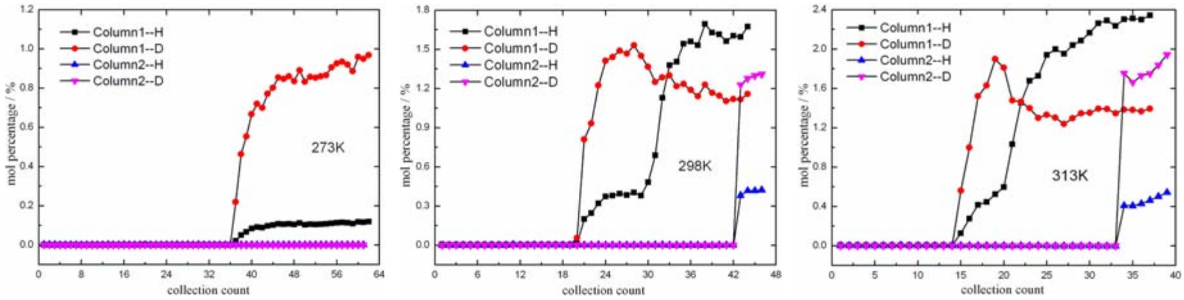

FIG.2. Content Change of H、D in the effluent gases at different column temperatures

Fig. 3 is the hydrogen isotope separation factor of column 1 with different temperatures. The affection on separation factor of temperature is evident. Because the hydrogen isotope effect of palladium is opposite to the temperature, the lower columns temperature is good for the H-D separation and then the H-D separation factor is higher, it had been validated by the results in Fig.3. At the lowest temperature of 273K, the average of H-D separation factor was 13.5. The hydrogen isotope content was 62.5%H-37.5%D in raw gas and reached 10.99%H-89.01%D after separation in column 1, so the deuterium was enriched.

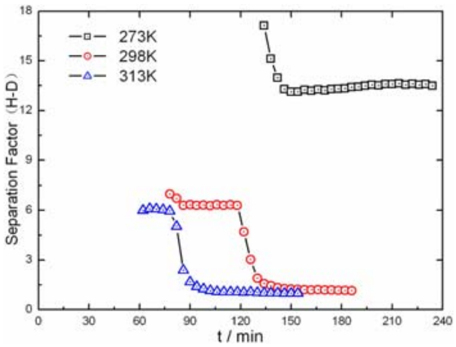

FIG.3. H-D separation factor of column 1 at different temperatures

3.2. Flux Dependence

Fig.4 shows the flux dependence of the separation for the raw gas mixture with 0.6%H_2-0.6%D_2-98.8%Ar, where the temperature was 298K and the fluxes were 3SCCM、10SCCM、15SCCM、25SCCM，respectively. The hydrogen isotopes didn’t elute from two columns in 150 min at 3SCCM. At 10SCCM, the hydrogen isotopes eluted from column 1 after 110 min and the deuterium content in effluent gases exceeded protium after 140min, but the hydrogen isotopes didn’t elute from column 2 in 160 min. When the flux was 15SCCM, the hydrogen isotopes eluted slowly from column 1 after 90 min and the deuterium content in effluent gases exceeded protium after 110min, the hydrogen isotopes suddenly eluted from column 2 after 140 min and the deuterium content exceeded protium. The protium content in the effluent gases was higher than deuterium at 25SCCM.

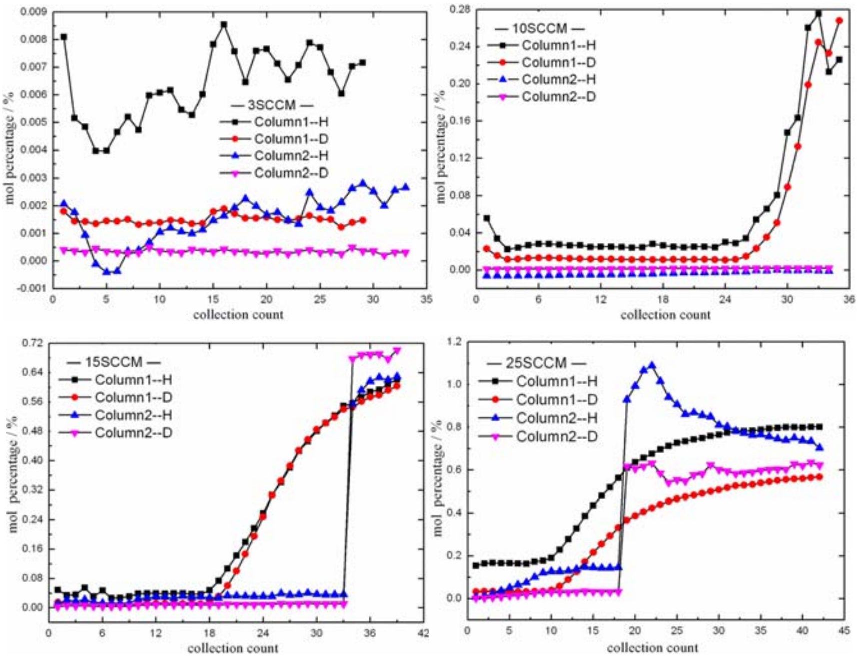

FIG.4. Content Change of H、D in the outflow with different fluxes of 0.6%H_2-0.6%D_2-98.8%Ar mixtures

Fig.5 is the separation for the 1.63%H_2-0.97%D_2-97.4%Ar mixture at 298K and the fluxes were 5SCCM、10SCCM，respectively. The flux of 10SCCM has been described in section 3.1. At 5SCCM, the hydrogen isotopes eluted from column 1 after 110 min and the deuterium content exceeded protium, but the hydrogen isotopes didn’t elute from column 2 in 160 min.

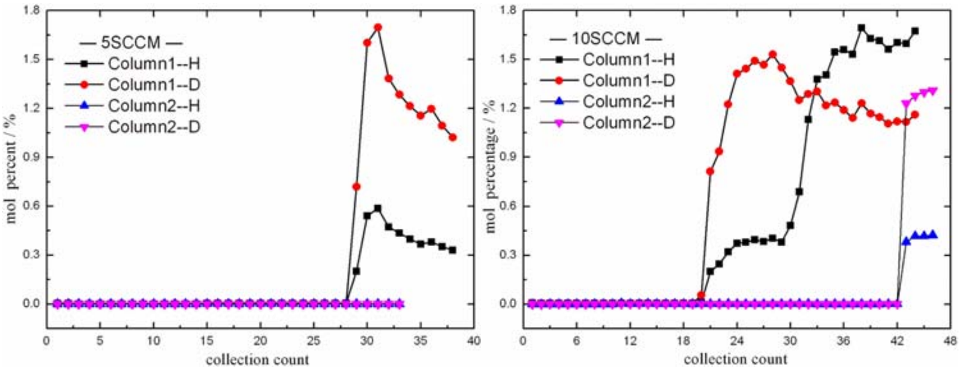

FIG.5. Content Change of H、D in the outflow with different fluxes of 1.63%H_2-0.97%D_2-97.4%Ar mixtures

These figures show that the flux can also affect the H-D separation. The flux too big or too small was disadvantage to H-D separation. When the flux was too big, such as 25SCCM, the diffusion played an important role, the hydrogen isotopes became diffusion but not displacement, so the lighter molecules ran faster than the heavier; the protium content was higher than deuterium in the outflow and the separation efficiency was very bad. When the flux was too small, such as 3 SCCM, it wastes too much time for the hydrogen isotopes eluting from the columns. As thus, the flux between 10~15SCCM was suitable for H-D separation when hydrogen isotope content was lower.

3.3. Hydrogen Isotope Content Dependence

Fig.6 summarizes the separation efficiency at 298K, where the flux was 10SCCM and the raw gases were 1.63%H_2-0.97%D_2-97.4%Ar 、 3.37%H_2-2.03%D_2-94.6%Ar and 5.0%H_2-3.0%D_2-92.0%Ar, respectively. The raw gas mixture 1.63%H_2-0.97%D_2-97.4%Ar has been described in 3.1 section. When the raw gas mixture was 3.37%H_2-2.03%D_2-94.6%Ar, the hydrogen isotopes eluted from two columns after 80 min, 150 min, respectively. As 5.0%H_2-3.0%D_2-92.0%Ar mixture, the hydrogen isotopes eluted from two columns after 64 min, 140 min, respectively. These figures show that the deuterium content in outflow exceeded protium in two columns. The results also indicated that the hydrogen isotopes eluted from columns faster with the increase of hydrogen isotope content in raw gas and the time column 1 waste was half of column 2.

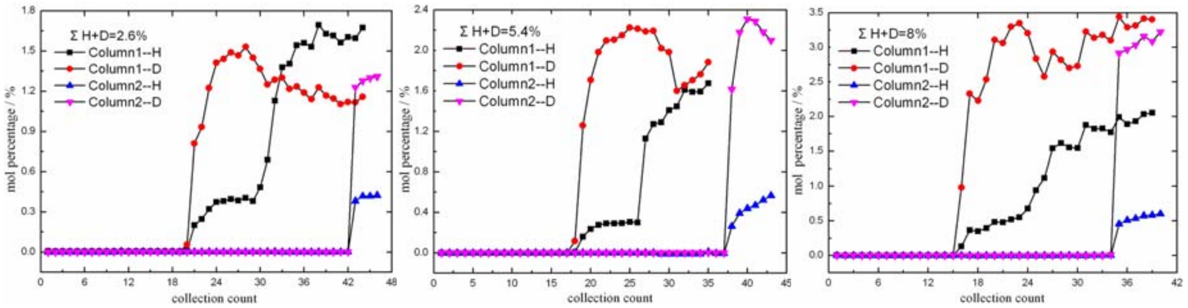

FIG.6. Content Change of H、D in the outflow with different hydrogen isotopes content in feed gases

Fig.7 is the H-D separation factor of column 1 at 298K with different the raw gases. The separation factor was increased when the hydrogen isotope content increased. Since the pressure of system was keep at 0.1MPa during experiment，when the hydrogen isotope content was small, the hydrogen isotopes injected in the columns could not reach the plateau pressure of H_2、D_2. At 298K, the plateau pressures of palladium absorption H_2、D_2 are 2.096kPa, 10.520kPa, respectively and the plateau pressures of palladium desorption H_2、D_2 are 0.710kPa, 3.830kPa, respectively [9]. When the hydrogen isotope content is higher, the amount of hydrogen isotopes is more; the pressure of hydrogen isotope will be close to the plateau pressure, so the H-D separation factor will be higher. It is also observed that the separation factor of 3.37%H_2-2.03%D_2-94.6%Ar mixture was higher than that of 5.0%H_2-3.0%D_2-92.0%Ar mixture at first equilibrium. This result indicated that the hydrogen isotope pressure is closer to the plateau pressure of palladium absorption or desorption H_2、D_2, the separation efficiency will be better. Therefore the protium and deuterium content within 6at% of raw gas would be suitable in these experiments.

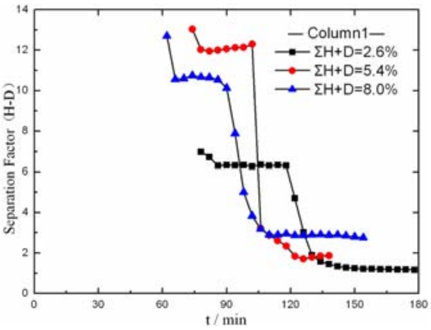

FIG.7. Separation factor of column 1 with different hydrogen isotopes content

4. Conclusions

A new type of chromatography for separation of H_2-D_2-Ar mixture has been developed using 63g Pd/K as functional material with two columns. The H-D separation was studied at different operation conditions including columns temperatures, the flux and hydrogen isotope content in raw gas. The influence of these parameters on separation factor was evident. The results showed that the separation of protium-deuterium would be better when protium and deuterium content in raw gas within 6at%, with a flux of 10SCCM and a lower columns temperature. When column temperature was 273K, raw gas flux was 10SCCM and hydrogen isotopes occupied 2.6at% of raw gas, the average separation factor of H-D was 13.5. Deuterium fraction defined as D/(H+D) of the first column was 37.5at% in the feed gas and was concentrated to 89.01at% after separation. The separation and enrichment of this chromatographic system is very good. If make many columns (more than two) cascade in any way to separation hydrogen isotopes, it can separate large-scale hydrogen isotopes expediently and continually. The new chromatographic separation has a potential for separation and recovery of hydrogen isotopes out of the tritium extraction systems in breeding Test Blanket Modules. The separation of H_2-D_2-Ar mixture below 273.15K and more details of the separation mechanism are now being investigated. They will be reported in the near future.

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