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GAS CHROMATOGRAPHIC SEPARATION OF HYDROGEN ISOTOPES USING METAL HYDRIDES

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Lawrence Livermore National Laboratory

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F.T. ALDRIDGE

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1 ABSTRACT

A study was made of the properties of metal hydrides which may be suitable for use in chromatographic separation of hydrogen isotopes. Sixty five alloys were measured, with the best having a hydrogen-deuterium separation factor of 1.35 at 60 degrees C. Chromatographic columns using these alloys produced deuterium enrichments of up to 3.6 in a single pass, using natural abundance hydrogen as starting material.

2 INTRODUCTION

The metal hydride chromatographic method of separating hydrogen isotopes makes use of the ability of some metals and intermetallic alloys to reversibly form solid metal hydrides when in contact with gaseous hydrogen at room temperature and pressure. Many of the deuteride analogues of these metal hydrides are less stable than the normal hydrides and therefore exhibit a higher hydrogen equilibrium pressure. If the stability difference is large enough and the equilibrium between hydrogen gas and hydride is sufficiently fast, a chromatographic column filled with a metal hydride forming metal can be used to separate deuterium from a deuterium-hydrogen mixture.

The method differs from the usual chromatographic technique in that no carrier gas is used. The chromatographic column is initially filled with argon. The deuterium-protium mixture is then forced slowly into one end of the column, pushing the argon out the other end. As the hydrogen stream enters the column it flows through hydride already saturated with hydrogen until it reaches unsaturated metal, where it is absorbed to form more hydride. As the hydrogen flows down the saturated part of the column, it isotopically equilibrates with the hydride and becomes more enriched in deuterium, while the hydride becomes deuterium-depleted. When this deuterium-enriched hydrogen gas reaches unsaturated metal and reacts it forms a hydride enriched in deuterium, which then further enriches the gas

passing over it. Thus the deuterium in the incoming hydrogen stream is concentrated at the boundary between hydrogen and argon as the boundary is pushed down the column. When the boundary reaches the bottom of the column, the first hydrogen gas to come off the column will be greatly enriched in deuterium. The boundary between hydrogen and argon remains sharp as it moves down the column because of reaction of hydrogen with unhydrided metal at the boundary prevents hydrogen from diffusing into the argon.

If the column is only partly filled with deuterium-containing hydrogen and this hydrogen is then pushed out with hydrogen which has been depleted of deuterium, all the deuterium can be concentrated in the hydrogen which first comes off the column. The maximum fraction of the column which can be filled with undepleted hydrogen depends on the gas-solid hydrogen isotope separation factor of the metal hydride. This fraction F is approximately

$$F = (S-1)/S \qquad (1)$$

where S is the separation factor, which is defined in Section 3.5.

Chromatographic separation of hydrogen isotopes was first reported by Glueckauf and Kitt in 1957 [1]. They used a column packed with a mixture of palladium black and asbestos. A single pass through this column was enough to concentrate the deuterium in a hydrogen mixture containing two percent deuterium into a band which contained over ninety percent deuterium. Palladium has a hydrogen-deuterium separation factor of two and easily forms reversible hydrides with gaseous hydrogen. This method of deuterium separation would be commercially superior to the methods now used if palladium were less expensive.

3 EXPERIMENTAL

3.1 MATERIALS

All the elemental metals used were commercially pure, with purities ranging from 99.9% for most of the metals to 99% for some of the rare earths. The gases were 99.9% pure, except for the deuterium which had an isotopic purity of 97%.

3.2 PREPARATION OF INTERMETALLIC COMPOUNDS

The intermetallic compounds were prepared by arc melting of the elemental metals in a water cooled copper boat under an argon atmosphere. Each of the samples was melted at least five times, with the sample being turned after each melting to insure homogeneity.

With some alloys an excess of the more volatile element had to be added so that the final alloy would have the desired composition. In a few alloys the volatility of the elements made arc melting impossible and samples were prepared with a muffle furnace by melting the elements in a zirconium carbide crucible under an argon atmosphere or sealed in a quartz ampoule. The composition of the samples was verified by atomic absorption analysis. Samples were annealed under argon for 24 hours at 800 to 1000 degrees centigrade. Five to ten grams were prepared for each run.

Kilogram quantities of some AB_5 type compounds were purchased from Nucor Corp. or Ergenics Corp., for use in column experiments.

Many of the compounds spontaneously fractured into a fine powder when they were hydrided and those which did not became so brittle that they could easily be powdered with a mortar and pestle. The powdered compounds oxidized rapidly on exposure to air, and were prepared and stored under an argon atmosphere. In some column experiments the intermetallic powders were size graded with sieves and only a selected size range was used in the column.

3.3 HYDRIDE PRESSURE-COMPOSITION ISOTHERMS

Pressure-composition isotherms were measured with the apparatus shown in simplified form in Figure 1. The volume of the part of the system labeled A was calibrated and could be changed by changing the auxiliary volume, labeled B. Both the auxiliary volume and the sample cell were made from high pressure stainless steel plumbing fixtures. Pressure was measured with a model DP-15 Validyne pressure transducer. After the sample was placed in the sample cell and the cell was evacuated and thermally equilibrated with an oil bath, the gas volume of the cell was measured by expanding argon gas from subsection A into the cell.

The cell was then evacuated again and the sample hydrided. Hydrogen was admitted to part A of the system, its pressure was measured, and it was expanded into the cell. The initial hydriding was usually slow, requiring several hours to several days at pressures up to 65 atmospheres. After several hydride-dehydride cycles were completed, the pressure composition isotherms were run. The pressure

transducer and the valves were interfaced with a Digital Equipment LSI-11 computer which ran the experiment.

An absorption isotherm was obtained by admitting a small amount of hydrogen through valve 1 into the calibrated volume, then opening valve 2 to allow the hydrogen to equilibrate with the sample. When the pressure became constant, valve 2 was closed and more hydrogen was admitted through valve 1. The process was continued until the equilibrium pressure had increased to a predetermined value. Usually the hydrogen pressure was increased by 0.1 to 0.2 atmosphere per step.

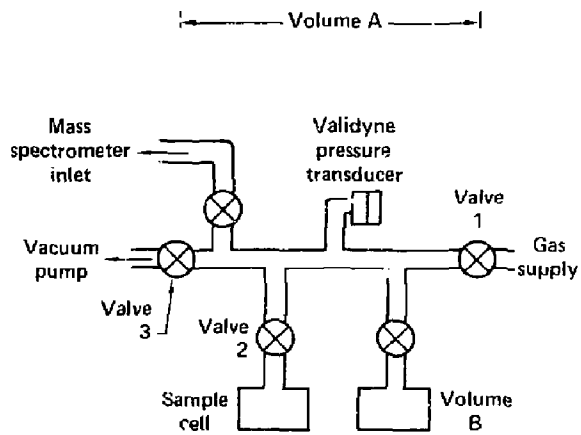

Figure 1 System for measuring pressure-composition isotherms

A desorption isotherm was then obtained in a similar manner by removing hydrogen from the calibrated volume in small increments through valve 3. The desorption-equilibrium cycle was repeated until all the hydrogen had been removed. The computer used the measured changes in pressure and the known volume of various parts of the system to calculate the total amount of hydrogen in the system after each step and the fraction in the gaseous and hydride phases. The computer also plotted the absorption-desorption isotherms. It took from two to twelve hours to obtain the data for each sample.

The system shown in Figure 1 was also used to measure the speed with which an intermetallic alloy absorbs hydrogen. The calibrated volume was filled with 65 atmospheres of hydrogen, valve 2 was opened, and the pressure was monitored by the computer until it became constant. The computer then calculated the time required for the hydride to reach various fractions of final saturation.

It was hoped that this type of experiment would provide some kinetic information about how fast hydrogen molecules dissociated at the hydride-gas interface and how rapidly hydrogen atoms diffused into the hydride. The hydriding speed was so strongly related to the equilibrium hydrogen pressure of the individual hydride being studied that kinetic conclusions could be drawn only in the few cases when hydrides with nearly equal equilibrium pressures were being studied.

3.4 DETERMINATION OF HYDROGEN ISOTOPE RATIOS

The apparatus for determining hydrogen isotope ratios is shown in Figure 2. The mass spectrometer is a Nuclide model 3-60-HD magnetic deflection type system equipped with dual

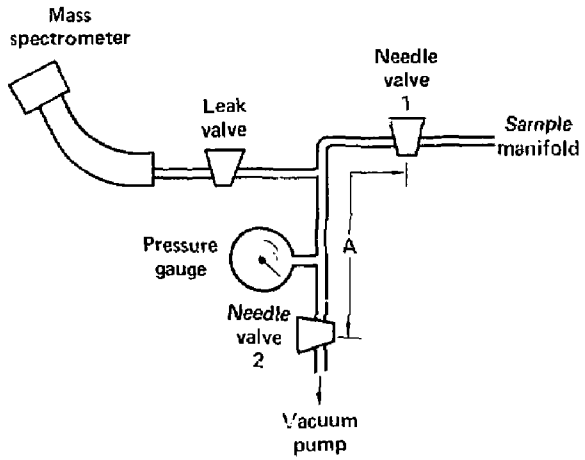

Figure 2 Mass spectrometer inlet system

Faraday cup detectors for simultaneous recording of masses two and three. The instrument is capable of recording natural abundance HD with a reproducibility of about one percent. It is equipped with a mercury diffusion pump and the sample gas was continuously pumped through it during a measurement. A gas sample to be analyzed was introduced into the volume marked A and the pressure adjusted to 0.2 atmosphere. The leak valve was then adjusted to give a pressure of 4×10^{-7} torr inside the mass spectrometer.

Some fractionation of H_2 and HD occurs at the leak valve. Experimental error due to this fractionation was minimized by always running the system with the same pressure at the leak valve inlet. An additional error was introduced by the formation of H_3^+ inside the mass spectrometer. This appears with HD as part of the mass 3 peak. The concentration of this ion fluctuated from day to day and was a function of both background pressure and hydrogen pressure within the mass spectrometer.

Both the fractionation and H_3^+ effects were compensated for by running a hydrogen standard through the mass spectrometer immediately after each run, using the same inlet pressure as the sample run and a range of mass spectrometer pressures above and below the sample pressure. A calibration curve was calculated from this data and the sample data was corrected using this curve.

3.5 DETERMINATION OF HYDRIDE SEPARATION FACTORS

The hydrogen isotope separation factor S is defined as the ratio

$$S = (D/H)_{gas} / (D/H)_{solid} \qquad (2)$$

in a closed system where hydrogen gas and a metal hydride are in equilibrium. In this study, which was done using hydrogen containing less than 0.1% deuterium, the separation factor was experimentally determined from the ratio

$$(HD/H_2)_{gas} / (HD/H_2)_{solid} \qquad (3)$$

which is the same as the ratio in Equation 2 when low deuterium to protium ratios are used. The $(HD/H_2)_{solid}$ in Equation 3 refers to hydrogen gas which has been desorbed from the hydride after equilibration. When the hydrogen is in the metal hydride, it is in atomic rather than molecular form.

Before a separation factor measurement, the hydride was allowed to equilibrate with gaseous hydrogen, at a pressure high enough to saturate the hydride, for at least 12 hours. A small amount of the gas was then drawn off and its isotopic ratio measured. The gas phase was then pumped off and the pumping continued until about half of the hydrogen was removed from the hydride. At this point the hydrogen being pumped from the hydride was trapped and used to measure the isotopic ratio of the hydride hydrogen. This method gave the same isotopic ratio for the hydride as would analysis of all the gas desorbed from the sample. Figure 3 shows the isotopic composition of the gas being removed from the hydride as a function of the fraction of the total hydrogen desorbed.

The isotopic ratio is constant until 95% of the hydrogen has been removed for all the AB_5 compounds tested. Palladium hydride behaves in a different manner, with the deuterium concentration decreasing monotonically as the hydrogen is depleted. The isotopic ratio of the hydrogen from palladium hydride could not be determined by measuring the hydrogen trapped after half of the hydrogen had been removed. With palladium all the hydrogen desorbed had to be trapped and analyzed since its isotopic ratio changed as the desorption progressed.

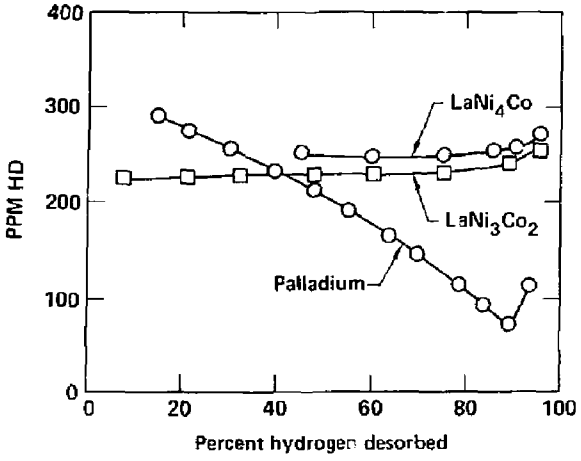

Figure 3 Deuterium content of hydrogen removed from metal hydrides

3.6 SEPARATION COLUMNS

3.6.1 PREPARATION OF THE COLUMNS

The columns were made of heavy-walled brass or stainless steel tubing with a maximum length of 75 centimeters. Columns longer than 75 centimeters were made of multiple 75 centimeter sections. The sections were joined with Swagelok fittings and could be sealed at each end so that air would not enter during filling. Before a column section was filled with hydride it was evacuated, filled with argon, and then sealed. The column was then placed in an argon atmosphere

inside a glove bag, opened, and filled with hydride powder. As it was filled it was tapped to insure good packing. If spacers were used they were dropped down the column each time a measured amount of hydride mixture was added. After each column section was filled, it was sealed before the glove bag was removed so that the hydride was never exposed to air. In columns where the hydride was mixed with other material, the mixing was done by placing all the components in a glass bottle under argon and turning the bottle until the material was uniformly mixed.

After the column was prepared it was placed in a thermostated oil bath and run through several hydride-dehydride cycles before measurements were made.

3.6.2 COLUMN ENRICHMENT EXPERIMENTS

The experimental apparatus for column deuterium enrichment experiments is shown in Figure 4. Experiments were run at pressures of 15 to 60 atmospheres. The column was first filled with argon at the desired pressure. Needle valve 1 was adjusted to provide the desired flow rate and needle valve 2 was adjusted to provide the standard 0.2 atmosphere pressure at the mass spectrometer leak valve inlet.

When the flow rate and system pressure were stabilized, the gas entering the column was changed from argon to hydrogen and the run was started. When hydrogen appeared at the bottom of the column the H_2 level rose to a steady value while the HD level rose to a peak due to its enrichment at the argon-hydrogen interface and then fell to a steady value. The ratio of the peak HD concentration to the steady-state concentration will be defined as the enrichment

factor, to distinguish it from the separation factor defined earlier. An example of a typical separation run is shown in Figure 5.

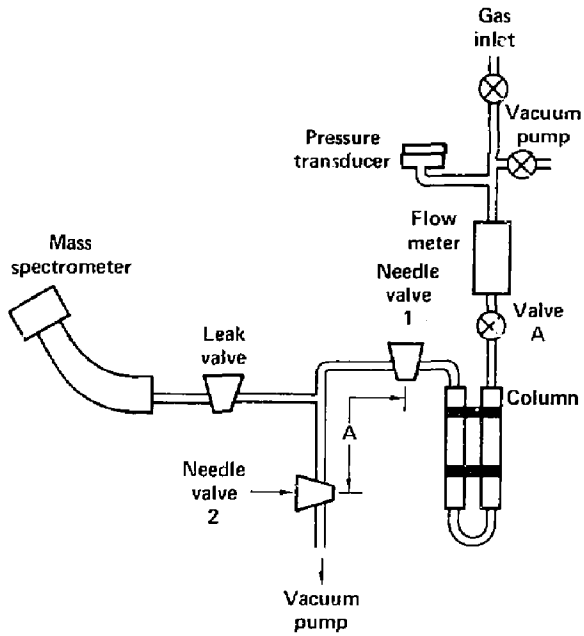

Figure 4 System for column enrichment experiments

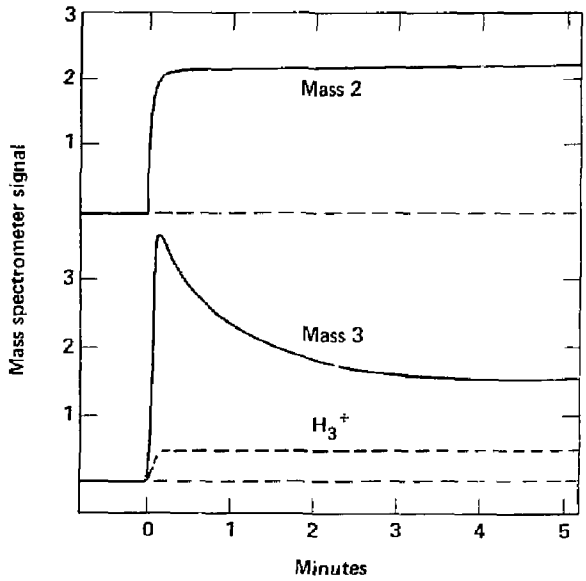

Figure 5 Column output of hydrogen isotopes vs time
30 inch $LaNiCo_4$ column at 100 degrees C

The mass three scale is a thousand times more sensitive than the mass two scale.

4 RESULTS

4.1 METAL HYDRIDE PROPERTIES

Many reversible metal hydrides were surveyed in a search for the best compounds to use in separation columns. Many of these have been investigated before but only a few of them have had previous measurements made of deuterium hydride properties or of separation factors. References to other work on these compounds are included in the tables. Most of the compounds were the AB_5 type where A is a rare earth or calcium and B is a transition metal. This type of intermetallic hydride was accidentally discovered in 1970 during research on rare earth cobalt magnets with the AB_5 crystal structure, and many other examples were quickly found [2].

4.1.1 LANTHANUM BASED AB_5 COMPOUNDS

$LaNi_{(5-X)}M_X$

Absorption isotherms for some of these compounds are shown in Figures 6 and 7. Other properties are summarized in Table 1. The column in the tables labeled "Hydrogen Atoms per Molecule not Removed" contains the amount of hydride hydrogen not removed by pumping on the sample for one half hour at 60 degrees C. The "Separation Factor" columns contain separation factors measured before and after multiple hydride-dehydride

cycles. This is explained in detail in Section 4.1.5.

$LaNi_5$. This has a larger hysteresis loop with deuterium than with protium. The curve is the closest of all the alloys studied to the theoretical flat plateau. The binary alloys usually have this type of curve while most of the ternary alloys have curves with sloped plateaus.

$LaNi_4Al$. Substitution of aluminum for part of the nickel gives a higher separation factor, a lower equilibrium pressure, and reduces the hydrogen capacity by a factor of two. The hydriding is very slow, as if the aluminum has poisoned the surface. Much of the hydrogen can not be removed at 60 degrees C during the desorption run. The hydrogen was desorbed between runs at about 200 degrees C. $LaNi_{4.5}Al_{.5}$ also has a much lower equilibrium pressure than $LaNi_5$, but the pressure is high enough for all the hydrogen to be removed during the desorption cycle.

$LaNi_4Fe$. This has an equilibrium pressure about half as high as $LaNi_5$ and a lower hydrogen capacity. A sample of $LaNi_2Fe_3$ absorbs four hydrogen atoms per molecule of metal but 70% of the hydrogen can not be removed at 200 degrees C.

$LaNi_4Zn$. This has deuterium and hydrogen isotherms which are almost identical. The zinc reduces the equilibrium pressure by sixty percent.

$LaNi_{(5-x)}Cu_x$

A series of compounds were studied with varied ratios of nickel to copper. All have a sloped plateau and a deuterium capacity which is less than the protium capacity. The equilibrium curves for these compounds are shown in Figures 8 and 9.

$LaNiCu_4$ has a separation factor of 1.32 at 60 degrees C. and was used in the first successful column isotopic separation experiments. Some samples were prepared with part

of the copper replaced with aluminum. These samples have lower hydrogen equilibrium pressures and higher separation factors, but equilibrate slowly and must to be strongly heated to remove all the hydrogen from them. Aluminum is known to lower the equilibrium pressure of AB_5 compounds [7][8].

TABLE 1

LANTHANUM BASED AB_5 COMPOUNDS AT 60 DEGREES C

COMPOUND	HYDROGEN ATOMS PER MOLECULE ABSORBED	NOT REMOVED	SEPARATION FACTOR BEFORE CYCLES	AFTER CYCLES	REFERENCES
$LaNi_5$	6.1	0.1	1.08	1.08	2,3,4,5,6
$LaNi_4Al$	3.8	2.7	1.29	-	7,8
$LaNi_{4.5}Al_{0.5}$	5.5	0.63	1.15	-	7,8
$LaNi_4Fe$	5.0	0.2	-	-	9
$LaNi_2Fe_3$	3.9	2.8	-	-	
$LaNi_4Zn$	5.8	0.6	-	-	9
$LaNi_3Zn_2$	4.3	1.5	-	-	
$LaNi_4Cu$	4.8	0.1	-	-	9,10
$LaNi_3Cu_2$	4.0	0.15	-	-	10
$LaNi_2Cu_3$	4.7	0.2	-	-	10
$LaNiCu_4$	3.5	0.2	1.32	-	10
$LaNiAlCu_3$	2.95	1.23	1.32	-	

TABLE 1 CONTINUED

LANTHANUM BASED AB_5 COMPOUNDS AT 60 DEGREES C

COMPOUND	HYDROGEN ATOMS PER MOLECULE ABSORBED	NOT REMOVED	SEPARATION FACTOR BEFORE CYCLES	AFTER CYCLES	REFERENCES
$LaNi_{0.5}Al_{0.5}Cu_4$	2.95	0.36	1.55	-	
$LaNi_2AlCu_2$	3.32	1.8	1.31	-	
$LaNi_{4.5}Co_{0.5}$	-	-	1.05	1.07	
$LaNi_4Co$	5.80	0.33	1.00	1.03	11
$LaNi_{3.5}Co_{1.5}$	-	-	1.04	1.03	11
$LaNi_3Co_2$	5.05	0.28	1.075	-	11
$LaNi_{2.8}Co_{2.2}$	5.37	0.02	1.13	1.12	
$LaNi_{2.7}Co_{2.3}$	5.18	0.09	1.15	-	
$LaNi_{2.6}Co_{2.4}$	5.42	0.13	1.18	-	
$LaNi_{2.4}Co_{2.6}$	5.45	0.12	1.12	-	11
$LaNi_{2.3}Co_{2.7}$	4.8	0.05	1.17	-	
$LaNi_{2.2}Co_{2.8}$	4.96	0.01	1.20	-	
$LaNi_2Co_3$	4.78	0.03	1.23	-	11
$LaNi_{1.5}Co_{3.5}$	4.28	0.13	1.28	-	11
$LaNiCo_4$	4.32	0.13	1.31	-	11
$LaNi_{0.5}Co_{4.5}$	3.94	0.46	1.29	-	11
$LaNi_{0.2}Co_{4.8}$	3.90	.51	1.25	1.23	
$LaCo_5$	3.40	0.44	1.20	1.16	11

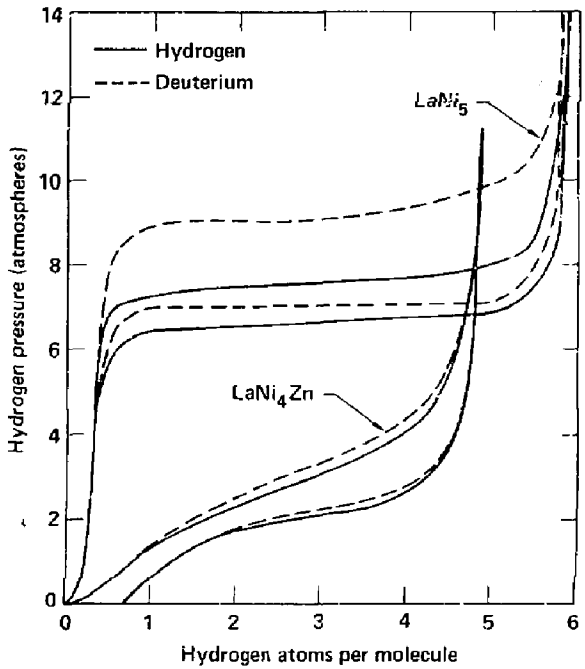

Figure 6 Pressure-composition isotherms for $LaNi_4M$ at 60 degrees C

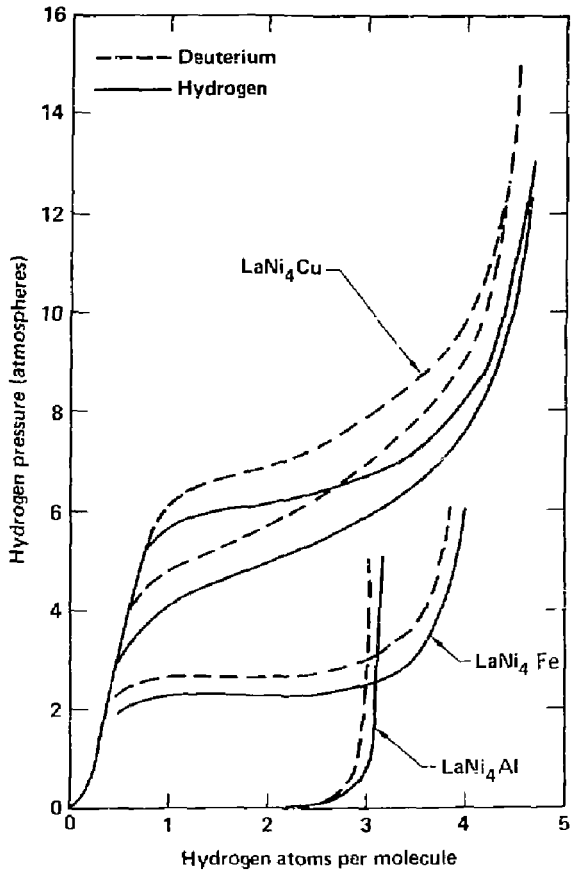

Figure 7 Pressure composition isotherms for $LaNi_4M$ at 60 degrees C

The $LaNi_4Fe$ and $LaNi_4Al$ curves are absorption isotherms.

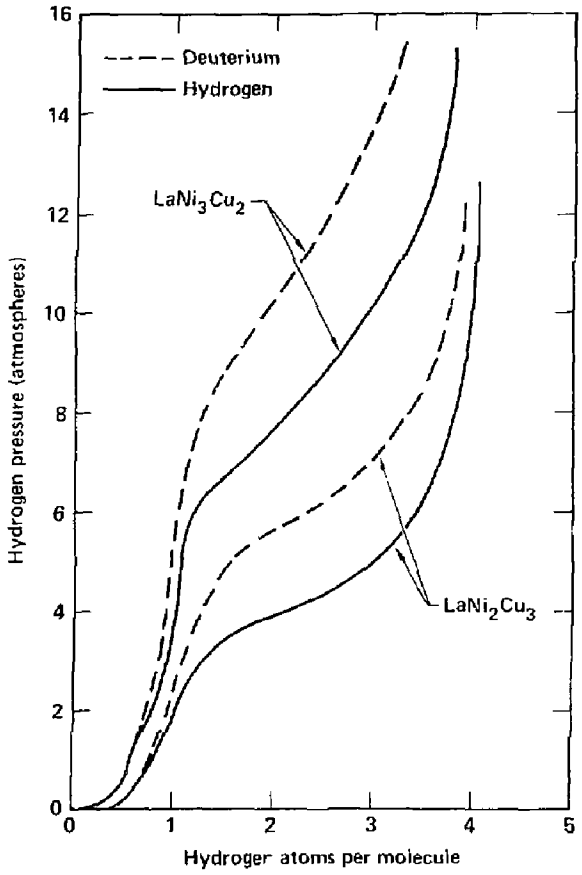

Figure 8 $LaNi_{(5-X)}Cu_X$ desorption isotherms at 60 degrees C

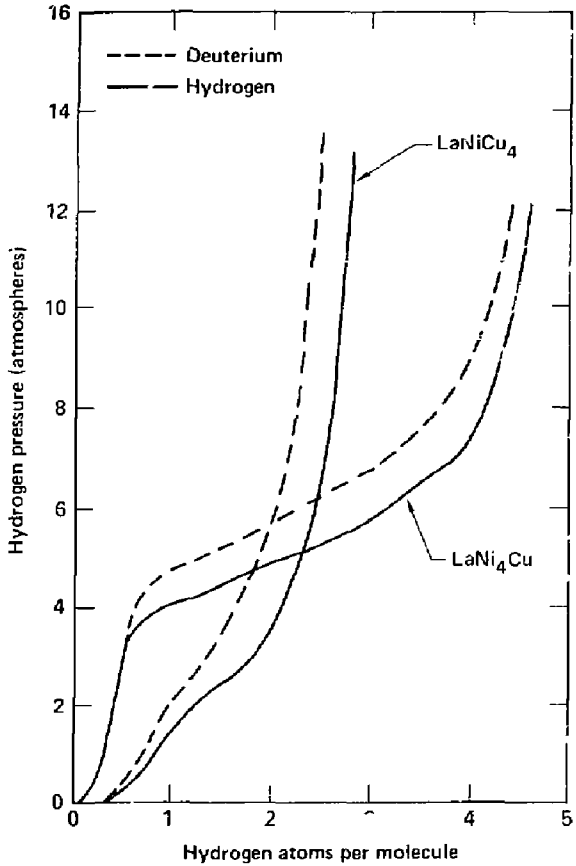

Figure 9 $LaNi_{(5-X)}Cu(X)$ desorption isotherms at 60 degrees C

$LaNi_{(5-x)}Co_x$

A series of compounds were studied with these compositions. The desorption isotherms for these compounds are shown in Figures 10 and 11. Separation factors were also measured for this series of compounds. They are shown in Figure 12. There is a sharp break in separation factor at a composition of $LaNi_{2.5}Co_{2.5}$.

These compounds were previously studied by Van Mal et. al. who measured desorption isotherms and crystal lattice parameters [11]. They showed that there is a sharp break in the crystal lattice parameters at a composition of $LaNi_{2.5}Co_{2.5}$, the same composition at which the separation factor discontinuity is observed here. The alloys rich in cobalt, including $LaCo_5$ show a two plateau desorption curve with the second plateau showing a twofold increase in equilibrium pressure when deuterium is substituted for protium [11][13]. The separation factors are much lower than these pressure ratios. The alloy $LaNiCo_4$ has the best separation factor of this group and was used in many column experiments.

The deuterium-to-hydrogen plateau pressure ratios measured from the curves do not correlate well with the measured separation factors. For example, Figure 11 shows that the ratio of deuterium to hydrogen plateau pressures is 1.27 in $LaNi_4Co$ hydride and is 1.10 in $LaNi_{2.8}Co_{2.2}$ hydride. The measured separation factors are 1.03 for $LaNi_4Co$ and 1.12 for $LaNi_{2.8}Co_{2.2}$. The compound with the larger pressure ratio has the smaller separation factor.

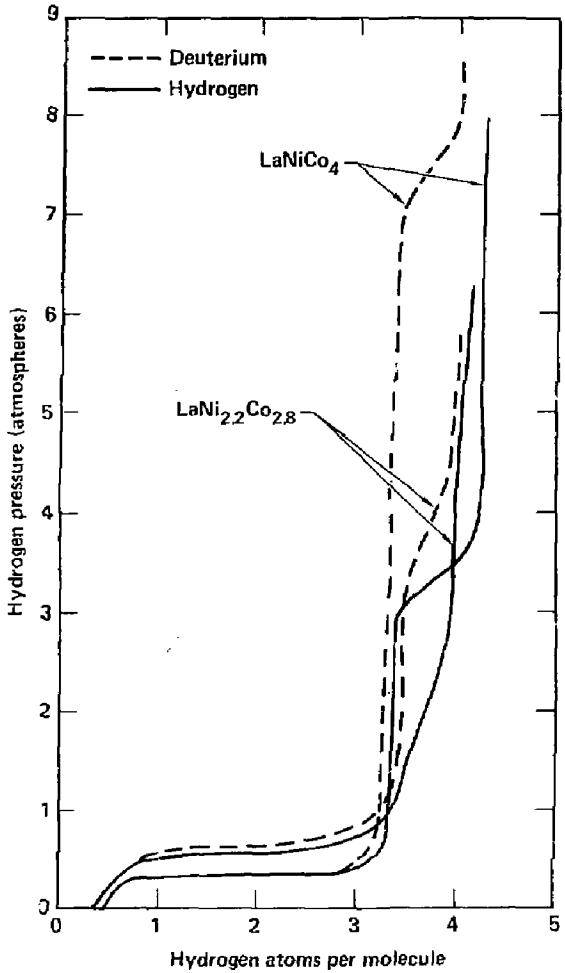

Figure 10 $LaNi_{(5-X)}Co_X$ desorption isotherms at 60 degrees C

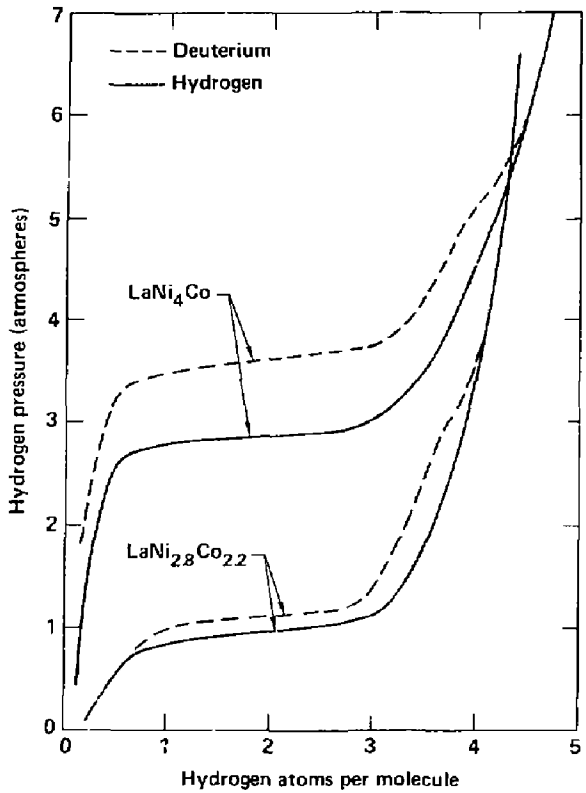

Figure 11 $LaNi_{(5-X)}Co_X$ desorption isotherms at 60 degrees C

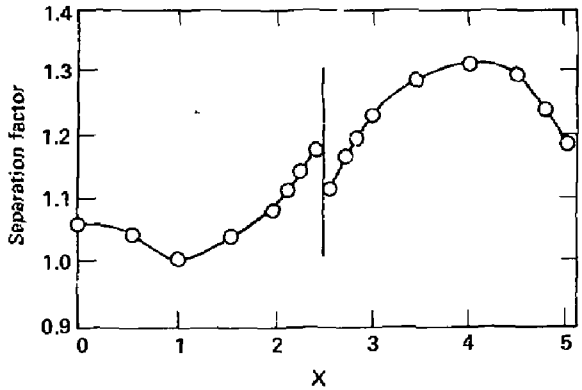

Figure 12 Separation factor vs $LaNi_{(5-X)}Co_X$ composition at 60 degrees C

4.1.2 CALCIUM BASED AB_5 COMPOUNDS

Many compounds of the general formula CaM_5 were prepared. All those which formed hydrides contained at least some nickel in the M component. Usually a better separation factor is obtained with compounds which are slightly calcium deficient, with a composition of about 0.8-0.9 calcium atom per molecule.

$CaNi_5$ has a large hysteresis loop and a two step plateau, with about five hydrogen atoms absorbed per molecule. Its separation factor is extremely variable from sample to sample, ranging from 1.06 to 1.20. Many compounds

were prepared where part of the nickel was replaced with other elements. Most of the substituted compounds are not as satisfactory as $CaNi_5$ for use in separation columns, with lower hydrogen capacities, lower separation factors, and in some cases slower absorption and desorption times. A summary of their properties is shown in Table 2, and a comparison of some of their desorption isotherms is shown in Figure 13.

A series of compounds with the general formula $CaNi_{(5-X)}Cu_X$ were prepared. $CaNi_4Cu$ has a higher and more reproducible separation factor than $CaNi_5$. $CaNi_3Cu_2$ has about the same separation factor as $CaNi_4Cu$, but it has a lower equilibrium pressure curve, making it harder to remove all the absorbed hydrogen, and it equilibrates slowly. $CaNi_4Cu$ and $Ca_{.8}Ni_4Cu$ were used in column separation experiments, which are described in section 4.2.

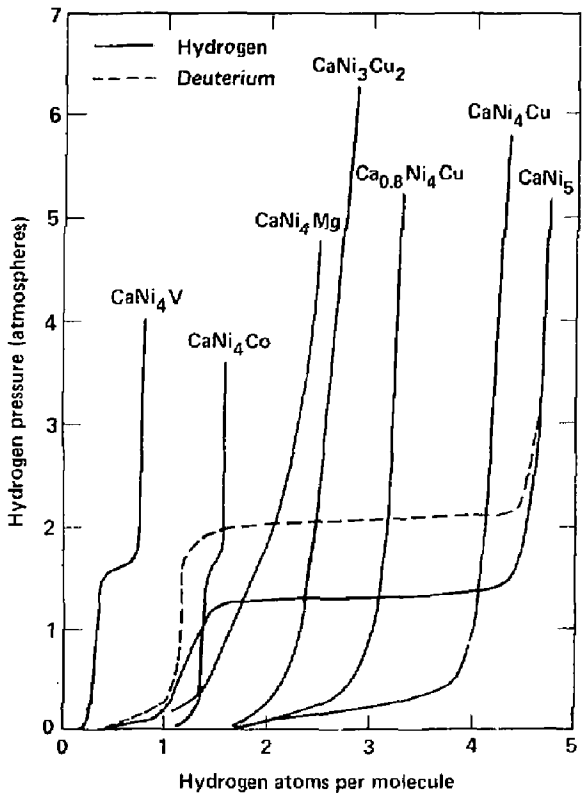

Figure 13 Desorption isotherms of some calcium based alloys at 60 degrees C

TABLE 2

CALCIUM AB_5 COMPOUNDS AT 60 DEGREES C

COMPOUND	HYDROGEN ATOMS PER MOLECULE ABSORBED	NOT REMOVED	SEPARATION FACTOR BEFORE CYCLES	AFTER CYCLES	REFERENCES
$CaNi_5$	5.27	0.03	1.05	1.13	10,12,13
$CaNi_4Al$	1.62	1.16	1.37	-	
$CaNi_4Si$	1.15	0.79	1.08	-	
$CaNi_4Cr$	1.25	0.66	1.19	-	
$CaNi_4Ti$	0.70	0.19	1.02	-	
$CaNi_4V$	0.94	0.14	1.14	-	
$CaNi_4Mn$	2.11	1.59	1.11	-	
$CaNi_4Co$	1.83	0.65	1.20	-	
$CaNi_{4.5}Co_{0.5}$	4.05	0.50	1.04	1.14	
$CaNi_{4.5}Mg_{0.5}$	5.42	2.62	1.05	-	
$CaNi_{4.5}Mo_{0.5}$	3.18	1.35	1.04	-	
$CaNi_{4.5}Al_{0.5}$	3.19	1.45	1.35	-	
$CaNi_4Mg$	4.60	0.58	1.15	-	
$CaNi_{4.5}Cu_{0.5}$	4.55	0.38	1.07	1.20	14
$CaNi_4Cu$	5.12	0.77	1.12	1.32	14
$CaNi_{3.5}Cu_{1.5}$	4.59	0.77	1.16	1.27	
$CaNi_3Cu_2$	3.74	0.63	1.17	1.23	
$Ca_{0.8}Ni_5$	3.50	0.06	1.03		
$Ca_{0.8}Ni_4Cu$	3.73	0.21	1.07	1.30	14
$Ca_{0.8}Ni_3Cu_2$	2.95	0.38	1.19	1.27	
$Ca_{1.2}Ni_4Cu$	6.16	2.43	1.09	1.30	
$Ca_{1.2}Ni_3Cu_2$	4.69	2.29	1.15	1.23	

4.1.3 OTHER AB_5 COMPOUNDS

Attempts were made to improve hydride performance by substituting other elements for part of the lanthanum or calcium in the A part of the alloy.

Substitution of cerium for part of the calcium in $CaNi_4Cu$ or $Ce_{0.8}Ni_4Cu$ increases the equilibrium pressure and reduces the fraction of the hydrogen which could not be easily pumped off, but it also decreases the separation factor. An attempt was made to use $Ca_{.6}Ce_{.2}Ni_4Cu$ in a column but its equilibrium pressure was too high for satisfactory column operation.

Substitution of zirconium for part of the calcium reduces both the equilibrium pressure and the separation factor. The use of mischmetal or cerium-free mischmetal for the A part of the compound always gives separation factors near unity. Similarly, the use of lanthanum-calcium mixtures gives compounds with separation factors which are too low to use for deuterium separation. These results are summarized in Table 3.

TABLE THREE

OTHER COMPOUNDS AT 60 DEGREES C

COMPOUND	HYDROGEN ATOMS PER MOLECULE ABSORBED	NOT REMOVED	SEPARATION FACTOR BEFORE CYCLES	AFTER CYCLES	REFERENCES
$Ca_{0.15}La_{0.85}Ni_5$	5.6	0.10	-	1.04	10
$Ca_{0.5}La_{0.5}Ni_5$	5.90	0.11	-	1.02	10
$Ca_{0.5}La_{0.5}Ni_4Cu$	3.89	0.03	-	1.12	10
$Ca_{0.8}Ce_{0.2}Ni_4Cu$	3.09	0.01	3.00	1.21	10
$Ca_{0.6}Ce_{0.2}Ni_4Cu$	4.28	0.08	1.03	1.23	
$Ca_{0.8}Zr_{0.2}Ni_4Cu$	3.33	0.24	1.09	1.27	
$Ca_{0.6}Zr_{0.2}Ni_4Cu$	2.59	0.16	1.04	1.22	
$MmCo_5$*	2.97	0.26	-	-	15,16
$MmCo_5$**	2.80	0.20	1.05	-	
$NiTi_2$	3.90	3.34	1.11	-	
$Zr_{0.8}Ti_{0.2}Mn_2$	2.85	0.32	1.07	1.07	17,18
$LaMg_2$	2.78	2.45	1.12	-	
Pd	0.78	0.3	1.60	1.56	1
$ZrMn_3$	3.63	0.49	-	1.03	

* Mm = mischmetal

** Mm = cerium free mischmetal

4.1.4 NON-AB_5 COMPOUNDS

FeTi and $CaMg_2$, and some other compounds of the same crystal types were studied in preliminary screening experiments. None of these compounds is useful for separation.

Palladium is already known for its hydriding properties and has been studied by many investigators. Its separation factor and pressure-composition isotherms were remeasured here to provide calibration for the apparatus and a baseline for comparison with other compounds. The separation factor found here for palladium is 1.55, while other investigators have found values near 2.0 [1]. The measurements reported here were made using hydrogen with natural abundance isotope ratios, while the previous investigators used deuterium concentrations which were two or three orders of magnitude higher. The data for palladium and the non AB_5 compounds are included in Table 3. Only the compounds which would form hydrides at 60 degrees C are included.

4.1.5 EFFECT OF REPEATED ABSORPTION-DESORPTION CYCLES

Many of the calcium based AB_5 compounds have separation factors which can not be reproduced from sample to sample. After many hydride cycles the divergent separation factors change and become much more reproducible. It has been shown that in $LaNi_5$ a surface segregation occurs in which lanthanum forms an oxide and nickel forms metallic clusters on the surface. This surface change continues during multiple

hydriding cycles, with lanthanum diffusing to the surface and oxidizing [19][20]. This change in $LaNi_5$ is seen at room temperature. A similar change occurs on the surface of FeTi but here a temperature of 200 to 400 degrees C is required [21][22]. It is thought that the nickel surface clusters catalyze the surface dissociation of adsorbed hydrogen gas.

Experiments with calcium AB_5 compounds show that separation factors change rapidly during the first hydriding cycles and then stabilize after about fifty cycles at a temperature of 100 degrees C. An example is shown in Figure 14. This stabilization occurs much more slowly at 60 degrees C, with some samples not reaching a stable separation factor after hundreds of cycles. The separation factors shown in Figure 14 were measured at 60 degrees C, but the cycling was done at 100 degrees C.

No change in separation factor with multiple cycles is seen with lanthanum compounds. If the separation factor change is due to the surface segregation occurring during multiple hydriding cycles, the change may not seen in lanthanum compounds because the segregation occurs at room temperature and the surface reaches a stable configuration quickly after the compound has been powdered by the initial hydriding reaction.

In calcium compounds the surface reactions may be slower, as in FeTi, and the greater atomic mobility brought about by higher temperatures and the lattice changes caused by hydriding may be needed to cause the postulated surface changes to occur. X-ray measurements of crystal lattice structure were made before and after multiple hydriding cycles had changed the separation factors. The lattice parameters were not changed by the multiple cycles. This suggests that the isotopic selectivity is connected with the dissociation and reassociation of molecular hydrogen as

catalyzed by nickel regions on the surface. On the other hand the calcium compounds usually had a lower hydrogen capacity after cycling, which would indicate that bulk changes had occurred. This decrease in capacity after many cycles has been seen with both $LaNi_5$ and $CaNi_5$ [12][23]. It is thought to be due to disproportionation of the hydrided alloy into lanthanum or calcium hydride and nickel metal.

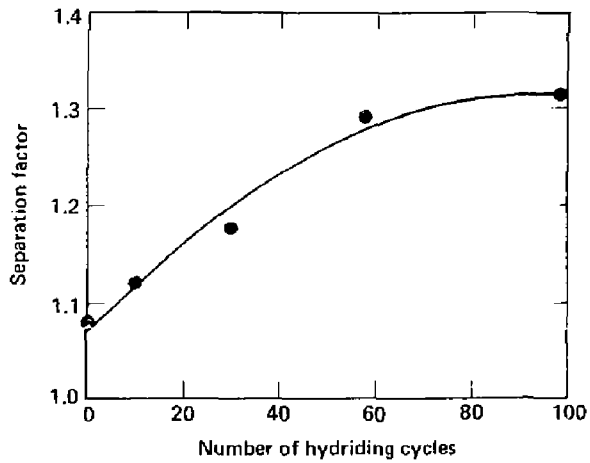

Figure 14 Separation factor of $CaNi_4Cu$ vs number of hydriding cycles

4.2 COLUMN SEPARATION EXPERIMENTS

4.2.1 $LaNiCu_4$

The first column experiments were run with a 6.5 millimeter diameter, 75 centimeter long column packed with $LaNiCu_4$. This column enriched the deuterium concentration by only a factor of 1.4. In later experiments the $LaNiCu_4$ was diluted with copper powder so that $LaNiCu_4$ was only 10% by weight. The same column filled with this mixture had an enrichment factor of 2.2. The added copper damped the temperature rise from the exothermic hydriding reaction and increased the ratio of gaseous to hydride hydrogen inside the column. With the added copper about 15% of the column hydrogen was in the gaseous state, while without the copper diluent, only 3% of the column hydrogen was gaseous.

Columns in which the $LaNiCu_4$ was diluted with powdered firebrick (instead of copper powder) gave enrichment factors which were the same as those obtained with undiluted $LaNiCu_4$. Since firebrick has a much lower density and thermal conductivity than copper it can not provide significant thermal damping but it does provide a higher gas to solid hydrogen ratio. This shows that the thermal damping effect is the more important one provided by the addition of the copper powder.

Maximum enrichment with $LaNi_4Cu$ columns was found at a pressure of 27 atmospheres and at a flow rate of 100 cc per minute of STP hydrogen. All the experiments with 6.5 millimeter diameter columns filled with various hydrides diluted 10 to 1 with inert material showed maximum

enrichments at flow rates between 100 and 200 cc per minute. This flow rate represents the traditional gas chromatography compromise between excessive back diffusion at slow flow rates and lack of complete equilibrium at high flow rates.

Maximum enrichment was found at a temperature of 80 degrees C for columns which contain $LaNiCu_4$. All the hydrides used in column experiments had separation factors which decrease as the temperature increased. The best temperature is a compromise between high separation factor at lower temperatures and faster equilibrium at higher temperatures.

A column with a length of 225 centimeters filled with the copper-$LaNiCu_4$ mixture had an enrichment factor of 2.4, only ten percent higher than that obtained in 75 centimeter columns.

4.2.2 $LaNiCo_4$

This gave much better results than $LaNiCu_4$. A 75 centimeter column with the $LaNiCo_4$ diluted to 10% with copper gave an enrichment factor of 2.6 under the best conditions. A 225 centimeter column filled with the same mixture had an enrichment factor of 3.6. The HD peak with the 225 centimeter column contained three times as much HD as the peak from the 75 centimeter column. The 225 centimeter peak was 2.5 times as wide as the 75 centimeter column peak. Both columns contained 5% of the column HD in the peak. $LaNiCo_4$ columns have their best enrichment factor at a temperature of 100 to 120 degrees C and a pressure of 55 atmospheres.

Mixtures of $LaNiCo_4$ and copper did not disperse evenly, with the $LaNiCo_4$ tending to clump and not disburse through the copper. This is probably because $LaNiCo_4$ is magnetic. Some columns were filled with a mixture of $LaNiCo_4$ and nickel

powder. This gave a more even dispersion of the hydride because nickel is also magnetic but did not improve the column performance. Either the uneven dispersion was not important or the effect of improving it was offset by the lower thermal conductivity of nickel.

4.2.3 $CaNi_4Cu$

The $CaNi_4Cu$ used in column experiments was run through enough hydride cycles to stabilize the separation factor before it was used to fill a column. Each packed column was also run through ten hydride cycles before it was used for separation experiments. $CaNi_4Cu$ does not work well as a column packing material. A 75 centimeter column packed with $CaNi_4Cu$ diluted to 10% with copper powder gave an enrichment factor of only 1.5 compared to 2.6 for the analogous $LaNiCo_4$ column. The $CaNi_4Cu$ column gave its best enrichment at a temperature of 125 degrees C. $CaNi_4Cu$ has about the same separation factor as $LaNiCo_4$ but a slower equilibration rate and a lower hydrogen equilibrium pressure. The slower equilibration rate probably accounts for the poorer enrichment factor.

4.2.4 OTHER COLUMN EXPERIMENTS

Many experiments were run with $LaNiCo_4$ columns in an attempt to improve column performance. To determine if the argon-hydrogen interface was flat or curved a column was prepared with several lumps of pure $LaNiCo_4$, undiluted with copper, around the outer edge of the hydride mixture a few centimeters from the top of the column. A centimeter nearer

to the top, another lump of $LaNiCo_4$ was placed in the center of the hydride mixture. When hydrogen flowed down the column the flow rate momentarily increased when the hydrogen hit the pure hydride in the center of the column, and then momentarily increased again by a larger amount when hydrogen hit the three lumps of pure hydride at the edge of the column.

When hydrogen flowed through the column in the reverse direction the same increases in flow were seen when the hydrogen reached the pure hydride, now located near the end of the reverse-flow column. The larger flow increase due to the edge pure hydride now came first. The time interval between the two flow increases was the same in both directions, indicating that the hydrogen-argon interface was flat across the column. If the interface had been moving down the column faster at the edge or center the time between the two flow increases would not have been the same in both flow directions.

The small gain in deuterium enrichment seen when column length is increased suggested that back diffusion was limiting column performance. An attempt was made to slow the back diffusion of deuterium by placing brass spacers in the column. The spacers were short cylinders with cone shaped ends and a diameter slightly less than the inside bore of the column. They were spaced evenly down the column so that a 75 centimeter column contained about 20 of them. The increased hydrogen velocity where the gas was forced to go around the spacer should decrease back diffusion past the spacers.

The actual columns made with spacers showed improvement, but the improvement was not dramatic. Column enrichment factors increased about 25%, and column performance still fell off drastically as column length increased. The columns could be run with about 30% lower flow rates than was

possible without spacers before performance fell off. This suggests that the column performance was being limited by back diffusion. The dramatic improvement in column performance as temperature was increased suggests that poor equilibrium was also a major limitation.

Thermal equilibrium may be another problem. The large heat of hydride formation can raise the hydride temperature so high that its hydrogen capacity is reduced. As the hydride cools it will absorb more hydrogen. Isotopic exchange and enrichment of the gas phase will not occur significantly until the hydride is essentially saturated. This will have an effect similar co slow isotopic equilibration, but with an opposite temperature dependence.

If the first hydrogen absorbed by a hydride forming material goes onto a site where it is more firmly bound than hydrogen absorbed when the hydride is already partly saturated, then these first sites will contain the hydrogen which is most enriched in deuterium. If these sites exchange more slowly with the gas phase, then the deuterium separation will be poorer. If these sites exchange too slowly, then the deuterium will be stripped out of the peak, exchanged back into the gas stream in a region where it is deuterium depleted, and essentially lost. To test this possibility a column run was made with 0.7 cc. of pure deuterium loaded onto the top of the column at the start of the run. The HD peak at the end of the run was six times higher and had an area fifty times larger than the area of a run without added deuterium. All the added deuterium was recovered in the HD peak. The deuterium added was less than 0.1% of the total amount of hydrogen needed to saturate the column.

The deuterium was not stripped from the front of the gas stream by any non-exchanging hydride sites. The HD peak was much broader at the bottom of the column, with the maximum HD

concentration in the peak only 0.3%, while the HD concentration at the top of the column was nearly 100%.

In another run, 4.5 cc of pure deuterium was loaded onto the top of the column at the start of the run. The maximum HD concentration at the bottom of the column was 1.1%, and the HD peak width was about the same as in the previous run. It is not possible to tell from these experiments if the peak broadening was caused by gas phase back diffusion or by slow equilibrium between the gaseous and hydride phases. These experiments do show that the peak broadening is not a function of the maximum HD concentration.

5 DISCUSSION

The column experiments produced individual enrichment factors of up to 3.6, but did not produce a large enough enrichment and did not concentrate enough of the column deuterium in the peak to be commercially practical. A practical column would have to extract about 30% of the column deuterium into the HD peak, and the peak would need an average enrichment factor of at least three. This would require a peak enrichment factor of about eight, instead of the 3.6 actually obtained. At the temperatures where the best enrichment was occurring the hydrides had separation factors of only 1.10 to 1.15. Equation (1) shows that only about 11% of the deuterium in the columns could theoretically be concentrated in the peak. Experimentally only 5% was concentrated there, because of incomplete equilibrium and back diffusion. This percentage did not change when longer columns were used.

In a commercially operating seperation plant the column would probably be partly filled with the amount of hydrogen from which the deuterium could be extracted and then this hydrogen would be pushed down the column with hydrogen which had been previously depleted. If only 5% of the column is filled with undepleted hydrogen, then the amount of hydrogen to be pumped is twenty times more than the amount to be depleted in deuterium. The cost of pumping and compressing this amount of hydrogen will make the method uneconomical [25]. A separation factor of 1.4 should require only four times more hydrogen to be pumped than the amount to be

depleted.

A plate type computer model of a column was used to calculate the effect on column performance of changing various column parameters. The model is described in the appendix. The model could simulate experiments by adjusting the separation factor, degree of plate equilibrium, back diffusion between plates, fraction of column hydrogen in the gas phase, and amount of residual hydride in the column before the start of a run. Calculations using this model suggest that both back diffusion and isotopic non-equilibrium are present to a large extent. The calculations show good agreement with experimental data. As an example, the results of a calculation are compared with a real column in Figure 15. The model column had a separation factor of 1.12, 70% equilibrium, 15% gaseous hydrogen, and 40% back diffusion. The experimental column was the same one used in Figure 5. It was a $LaNi_4Co$ column with 15% gaseous hydrogen and a separation factor of about 1.12 at the 100 degree temperature at which the run was made. The equilibrium and back diffusion percentages were adjusted in the calculation to give the best agreement with experiment.

Using the relations developed experimentally by Boser [24] for absorption and desorption rates of $LaNi_5$ as a function of temperature, and assuming that the equilibration rate follows the same temperature dependence, the percentage of equilibrium can be calculated as a function of temperature. The relative back diffusion rate can also be calculated as a function of temperature change, since the diffusion constant is proportional to the square root of temperature. These, along with the experimental separation factors measured at different temperatures, can then be used to model changes in column performance at different temperatures.

A comparison of experimental and calculated enrichment factors is shown in Table 4. The parameters in the calculation were adjusted to give the best agreement with experiment for the 75 centimeter column at 100 degrees C. These parameters were then used to calculate enrichment factors at other temperatures and with other column lengths. Only the 60 degree calculation shows a large deviation from the experimental result. The results show fair agreement with experiment, and the calculations show that at lower temperatures the increase in separation factor is offset by much poorer equilibrium. The experimental performance at lower temperature is poorer than the calculation predicts. This may indicate that isotopic equilibrium is slower than the data of Boser would predict. Diffusion effects are not significantly changed by temperature changes over the range used in these experiments.

TABLE 4

COMPARISON OF CALCULATED AND EXPERIMENTAL RESULTS

$LaNiCo_4$ COLUMN

TEMPERATURE	COLUMN LENGTH	ENRICHMENT FACTOR	
DEGREES C	CM	EXPERIMENT	CALCULATED
100	75	2.8	2.8
100	225	3.6	4.2
100	45	2.3	2.2
60	75	1.7	2.5
120	75	2.7	2.6

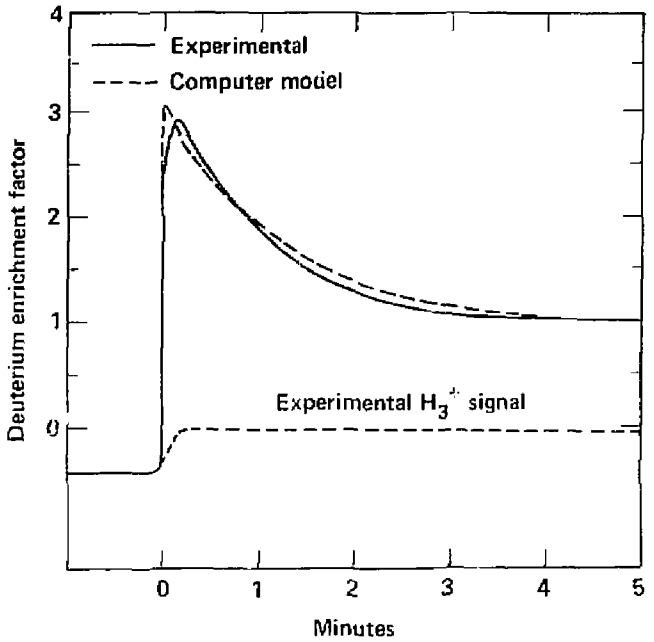

Figure 15 Comparison of experimental and calculated column performance

Incomplete desorption of hydrogen between column runs, with 5% of the hydrogen not desorbing had little effect on the column performance, according to the computer simulations. Since experimentally the amount of hydrogen not removed between runs was less than 5% at 100 degrees C, this is probably not a source of experimental error.

The computer model also shows that a column with a separation factor of 1.30 would function well with the

equilibrium and back diffusion conditions which did not produce satisfactory enrichments with a separation factor of 1.12, and that a column with a separation factor of 1.55 (i.e. palladium) would work superbly with only 50% equilibrium and with 60% back diffusion. The results of these calculations are shown in Figure 16. The performance of palladium in separation columns has, of course, been well shown experimentally [1].

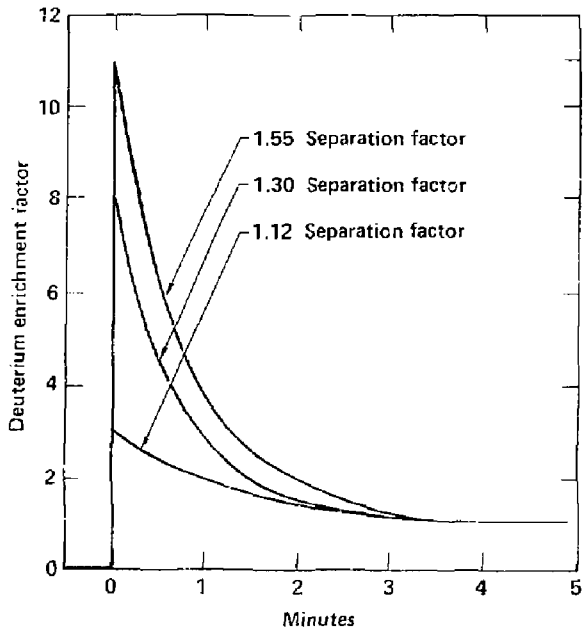

Figure 16 Calculated column performance

The conclusion to be drawn from this work is clear. Both experiment and computer modeling show that an economically attractive chromatographic hydride separation scheme is not possible using any of the hydride-forming alloys available at a commercially acceptable price. If a low cost alloy becomes available with a separation factor of 1.30 or better at the operating temperature required for rapid equilibrium, then the chromatographic method may be commercially successful. If an inexpensive alloy were found which matched the separative qualities of palladium, then commercial success would surely be assured.

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7 APPENDIX

COLUMN MODEL

A computer program was written to model the separation column, in order to study the effects of various parameters on column performance. A plate model of the column was used, since it could be easily adapted to computer calculations. The plates in the chromatographic column are mathematically analogous to the plates in a distillation column.

The column is treated as a succession of plates, with the gas and hydride phases being in equilibrium within each plate. The gas phase is allowed to flow between plates, while the hydride phase is stationary. The changing equilibria are calculated as the gas flows from plate to plate down the column.

Before the start of a calculation, values of separation factor, fraction of hydrogen in the gas phase, and the initial fraction of hydride saturation are entered. These values are usually chosen to match the known properties of experimental columns. Values for the fraction of equilibrium attained within a plate, and the fraction of hydrogen gas which back diffuses between plates, are also entered. These have not been experimentally measured.

At the start of a calculation, the first few plates are filled with hydrogen and the equilibrium between gas and hydride deuterium is calculated from the input parameters. The gas in each plate is then shifted one plate downstream, and the first plate in the column is filled with

unequilibrated gas.

The total amount of deuterium in each plate after the shift is calculated and distributed between gas and hydride, using the separation factor and fraction of equilibrium specified at the start of the calculation. After all the plates are re-equilibrated, part of the gas in each plate is exchanged with the next plate upstream to correct for back diffusion. The process is then started over, with each plateload of gas again shifted downstream.

The gas from the last completely filled plate flows into an empty or partly filled plate. When the process has been repeated enough times to fill the end plate, it is equilibrated and added to the calculation chain. The number of plates in the column grows larger as the calculation continues. This is equivalent to the experimental case where the length of column filled with hydrogen grows longer as the hydrogen-argon boundary moves down the column.

The calculations continue until the desired number of plates have been filled with hydrogen. At this point, the shifting of gas and re-equilibration continues to be calculated as before, but the gas from the last plate is pushed out of the column instead of into an empty plate.

A plot of the deuterium content of this numerically expelled gas is what is shown in Figures 15 and 16. The computer calculation gives enrichment factor as a function of number of plateloads of gas expelled from the column instead of time, as is shown in the figures. The comparison of calculated and experimental curves is obtained by dividing the total number of calculated plates filled with H_2 by the time required to fill the experimental column with H_2. This gives a value for the number of plates per minute, which is used to convert the calculated HD peak into a function of time. The temporal peak width is usually less than 10% of

the time required to fill the column in both the experiment and calculation.

When a calculation is being compared to an experimental run, the calculation is continued until the calculated and experimental enrichment factor are the same. The shape of the calculated and experimental HD peaks are then compared. If the shapes do not match, the calculation is repeated, with new values for the equilibrium fraction and back diffusion, until the best fit is found by trial and error.

When columns of different length are being compared, one column is adjusted for best fit, as above. The other column is then calculated using the same parameters, with the ratio of number of plates calculated the same as the ratio of the experimental column lengths.

When the same column is being run at two different temperatures the same number of plates is used for each calculation, with one column simulation adjusted for best fit. The column parameters are then changed to allow for the expected effect of temperature and the column calculation is rerun without any more adjustment of parameters.

The program can also simulate cases where part of the column is filled with hydrogen before the start of the calculation, and this hydrogen is then pushed down the column with hydrogen containing a different fraction of deuterium. This simulates the scheme where the column is partly filled with normal abundance hydrogen, and then deuterium-depleted hydrogen is used to push the normal hydrogen down the column.