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# HYDROGEN ABSORPTION PROPERTY OF ENCAPSULATED $\text{LaNi}_{4.25}\text{Al}_{0.75}$

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**Key Words:** metal hydride silica separation

**Abstract:** For hydrogen economy to become a reality, hydrogen production will have to be greatly increased from what it is today. Hydrogen will have to be recovered from a variety of gas streams including low concentration streams with efficient methods. Efficient process for recovering hydrogen in low concentration streams is not available today. Powder of  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  was encapsulated in a porous silica matrix to produce a stable composite material. The material was packed in a column and tested for hydrogen absorption from streams containing nitrogen, methane or carbon monoxide. The composite material removed hydrogen from nitrogen containing methane very well, but suffered decrease in capacity and rate when carbon monoxide was present. Using fluorinated metal hydride powder improved the kinetics but not the tolerance to carbon monoxide.

## 1. Introduction

Hydrogen is certainly a clean fuel, but there is no significant quantity of naturally free hydrogen anywhere on earth. Hydrogen exists mostly in combined form with other elements, such as in water and hydrocarbons. Energy is required to free hydrogen from these compounds before it can be used as a fuel. This energy requirement must be minimized to maximize the net useful energy carried by hydrogen. Hydrogen demand today is mostly in the chemical industry and the petroleum refinery industry. This demand for hydrogen is met by steam reforming of hydrocarbon gases and partial oxidation of hydrocarbon liquids and coal. The cost of hydrogen produced in this way is very low compared to the value of the products made. Many off-gas streams containing up to 50% hydrogen are discarded for economic reasons. Hydrogen produced today is less than a few percent of what will be needed in a hydrogen economy. In the envisioned hydrogen economy hydrogen will be produced from multiple sources that include renewable and non-renewable. Low hydrogen content streams will not be discarded and the hydrogen will be recovered using cost-effective recovery techniques.

Present technologies for hydrogen separation include pressure swing adsorption (PSA), cryogenic and membrane processes. All three processes are efficient for high hydrogen content and high-pressure feeds, and are not efficient for low hydrogen content and low-pressure feeds. For PSA, the inefficiency is partly due to the fact that the adsorbents, that include molecular sieves and activated carbons, preferentially adsorb the heavy impurities. This makes the process less efficient when the heavier components to adsorb are more than about 50%. In such case an adsorbent that adsorbs hydrogen instead of the heavier components will be more efficient. Hydrogen adsorbent that can be used in a practical separation process is not available today. The goal of this work is to develop such an adsorbent.

## 2. Metal Hydride Could Be An Ideal Hydrogen Absorbent

It is well known that a group of metal alloys can absorb hydrogen reversibly under moderate temperature and pressure to form metal hydrides. An example is  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  (LANA.75), which is used in this work. This metal hydride can absorb hydrogen up to about 6 mmol/g depending on temperature and pressure. See Figure 1. The absorbed hydrogen can be recovered by heat or/and evacuation. However, attempts to use this type of material to separate hydrogen from other gases runs into two practical problems. First, the material breaks down to a fine powder after a few absorption/desorption cycles. The powder form makes it inapplicable in a separation column, because the powder self compacts then blocks gas flow. Second, the material is sensitive to reactive impurities such as oxygen and carbon monoxide. A small amount of these impurities in the feed gas renders the material inactive to hydrogen. These two problems, one physical and the other chemical, must be overcome in order to use metal hydride for hydrogen separation. Examples of past work in this area are given in references 1-2.

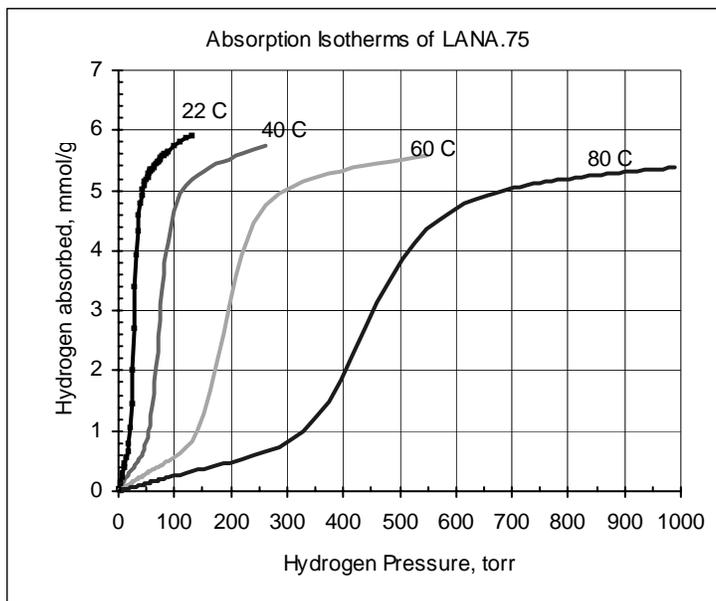


Figure 1. Hydrogen absorption isotherms of  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  (LANA.75).

## 3. Encapsulation Of Metal Hydride

It was reported earlier that metal hydride powder could be encapsulated in a porous matrix of silica to produce a composite material in granular form [3]. The granules consisted of small metal hydride particles uniformly distributed in a porous matrix of silica. They stayed physically intact for over 100 absorption/desorption cycles. It was reasoned that the expansion and contraction of the metal hydride particles did not break up the granules because the particles occupied a relatively small fraction of the matrix. For example, a composite sample containing 50 wt% of  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  has only 15 vol% of the metal hydride. The composite material provided another advantage. The pores of the matrix could be adjusted to permit the small hydrogen molecules to reach the metal particles



Figure 2. Pictures of (a)  $\text{LaNi}_{4.75}\text{Al}_{0.25}$  as received, (b) after 10 absorption/desorption cycles, (c) Granules of silica encapsulated  $\text{LaNi}_{4.75}\text{Al}_{0.25}$  after 100 cycles.

but to deny passage to the larger size impurities, and therefore protect the metal hydride particles from the impurities. For this work, samples were prepared with the same method and then packed in a small column for testing in a flow through arrange. These tests characterized the material's ability to remove hydrogen from a flowing gas stream containing nitrogen, methane and carbon monoxide. The sample preparation steps are briefly reviewed here: (1) Break down the metal hydride, LANA.75, particles to less than 20 micron by repeated hydrogen absorption/desorption and sieving. (2) Prepare a sol of fumed silica or Tetraethyl Orthosilicate (TEOS). (3) Mix and suspend the metal hydride particles in the sol until the mixture gels and solidifies. (4) Dry and granulate the final product. Using these general steps, two variations were produced and evaluated: (1) Composite granules were dip coated and dried three times with a solution of tetraethyl orthosilicate; this is sample 6B. (2) The LANA.75 powder was first fluorinated before encapsulated; this sample 12B. The fluorination on LANA.75 followed the procedure given in reference 2. The sol of fumed silica was prepared by mixing fumed silica with water in proportions of one gram silica to five gram water. The sol of Tetraethyl Orthosilicate was prepared by mixing TEOS, water and ethanol in proportions of one gram TEOS, 18 gram water and 4 gram ethanol. Granules of silica encapsulated  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  is shown in Figure 2 together with as received  $\text{LaNi}_{4.25}\text{Al}_{0.75}$  and its powder after absorption/desorption cycles.

#### 4. Test Apparatus And Procedure

The test apparatus consists of a U-shaped column, gas supplies with mass flow controllers, a pressure control valve, a TCD (thermal conductivity detector), thermocouples, pressure transducers and a computer data logging system. The U-shape column is fabricated from a  $\frac{3}{4}$ -inch (1.9-cm) diameter, 6-inch (15.2-cm) long stainless steel that can hold 40 cc of sample for test. The mass flow controllers control the flow rates of different gases to make a feed stream of target compositions. The gases for feed are hydrogen, nitrogen, 10% methane in nitrogen, and 1% carbon monoxide in nitrogen. Down stream of the column, a pressure control valve maintains the system pressure at target values. A side

stream flows at constant rate through the TCD that measures the exit hydrogen composition continuously. See Figure 3 for a photo and schematic of the experimental apparatus.

Encapsulated metal hydride granules of 0.60 to 0.84 mm size are loaded in the U-shape column for

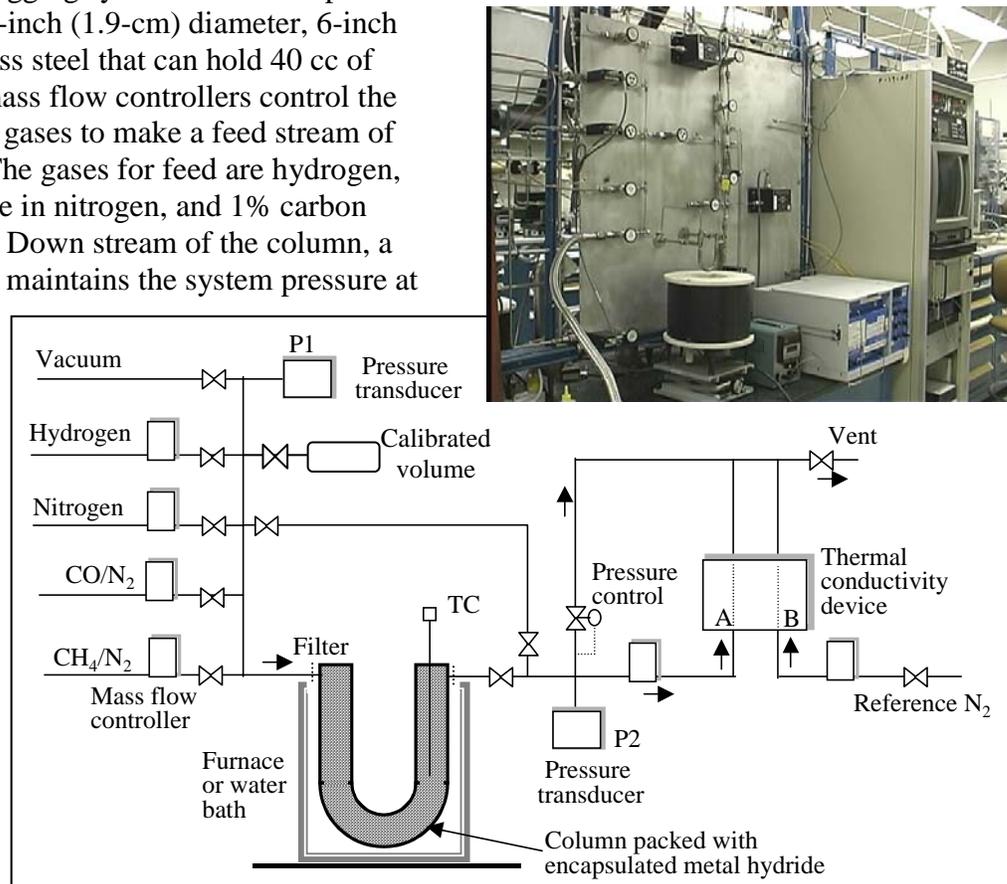


Figure 3. Photo and schematic of experimental apparatus.

flow-through tests. Each sample packed in the column is first activated to bring up its reactivity toward hydrogen. Activation involves bake out at 120 °C to remove volatile materials and repeated hydrogen absorption/desorption until the absorption kinetics approaches a limit. After activation, a series of flow through tests is conducted. Each flow through test consists of an absorption step and a regeneration step. In the absorption step, the feed stream of target composition flows into the column. Hydrogen is absorbed and the rest continue through the column. The exit gas hydrogen concentration is measured continuously by the TCD. The flow continues until the column is saturated when hydrogen concentration at the exit equals the feed. A breakthrough curve of hydrogen concentration is produced.

The breakthrough curve is a manifestation of the capacity and kinetics of the packing material. In the regeneration step, nitrogen at a target flow rate is metered through the column and the column is heated to 120 °C. hydrogen is desorbed and carried out by the nitrogen to the TCD for measuring the concentration. The hydrogen concentration curve during regeneration shows the pressure and the amounts of hydrogen that is recovered.

## 5. Experimental Results

### 5.1. Activation

Sample in the column was heated to 120 °C under vacuum for about one hour or until all volatile components are removed. The sample was then exposed to known amount of hydrogen at 3500 torr. Hydrogen absorption would begin in a few minutes or longer depending on the sample. After saturation the hydrogen was desorbed at 120 °C with evacuation. The process was repeated 2 to 5 times till the absorption rate was fast and approached a limit. All the samples tested exhibited equal or easier activation compared to the original metal hydride powder. Figure 4 shows the absorption rate of sample 6B up to cycle 6. The 90% saturation time decreased from hours to minutes after six cycles. Pretreatment of the metal hydride powder with fluorination, using a method described in reference 2, improved the initial kinetics very significantly. The absorption rate of 12B, an encapsulated

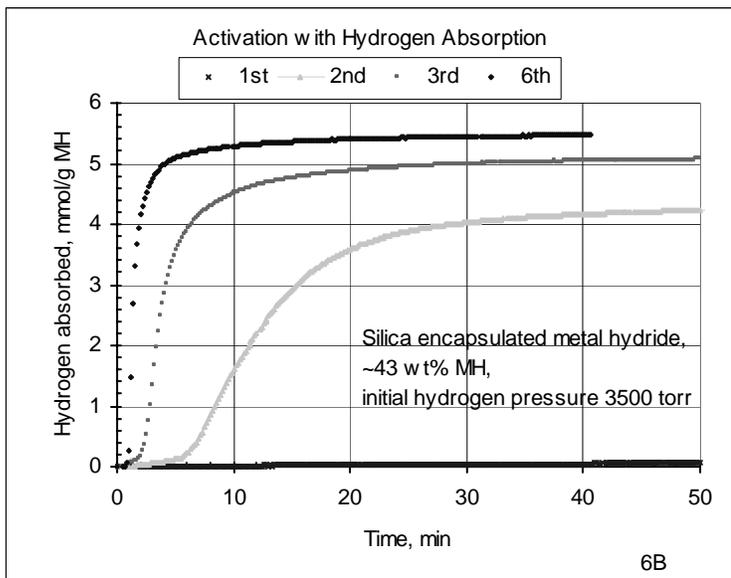


Figure 4. Activation of encapsulated and dip coated sample 6B.

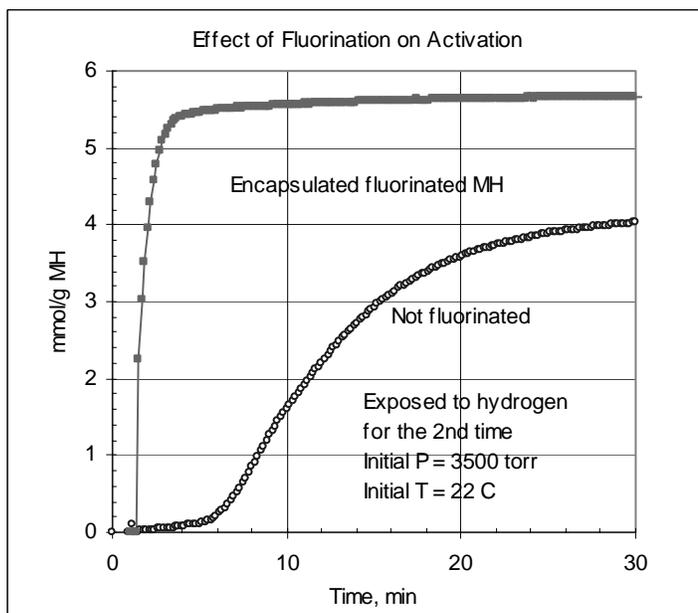


Figure 5. Activation of encapsulated fluorinated sample 12B compared to 6B.

fluorinated sample, reached saturation in minutes in the second cycle, while that of 6B took over an hours. See Figure 5.

## 5.2. Absorption From H<sub>2</sub> And N<sub>2</sub> Mixture

Each flow-through test begins with pure nitrogen feed at 50 cc/min to establish the system pressure and the concentration baseline for the TCD. The feed is then switched to hydrogen and nitrogen at target flow rates. The streams are jointed in a 0.5-cm diameter, 30-cm long stainless steel tube to form a mixture feed before entering the column. In the column hydrogen is absorbed by the encapsulated metal hydride (the packing material), and the rest continues to flow through. Gradually a concentration profile called the absorption front is established, with high concentration at the entering end and low concentration at the exit end. When this concentration profile exits the column, an S-shape “breakthrough” curve is generated.

The width of the breakthrough curve displays the performance of the packing material. A narrow breakthrough curve indicates favorable kinetics. The concentration profile also shows the hydrogen capacity of the packing material under the test conditions. A concentration profile of sample 6B is shown in Figure 6. The profile shows that for the first 280 minutes the column removed most of the hydrogen from the feed. The concentration was reduced from 14.4% to as low as 1%. The breakthrough curve began at 280 minutes and completed at 380 minutes, covering a period of 100 minutes. This is an equivalent of about ¼ of the length of the column. The amount of hydrogen absorbed is also shown in this figure as a function of time. At total breakthrough the column absorbed 5.5 mmol/g of metal hydride in the packing material. This is approaching the fully saturated value of 5.8 mmol/g.

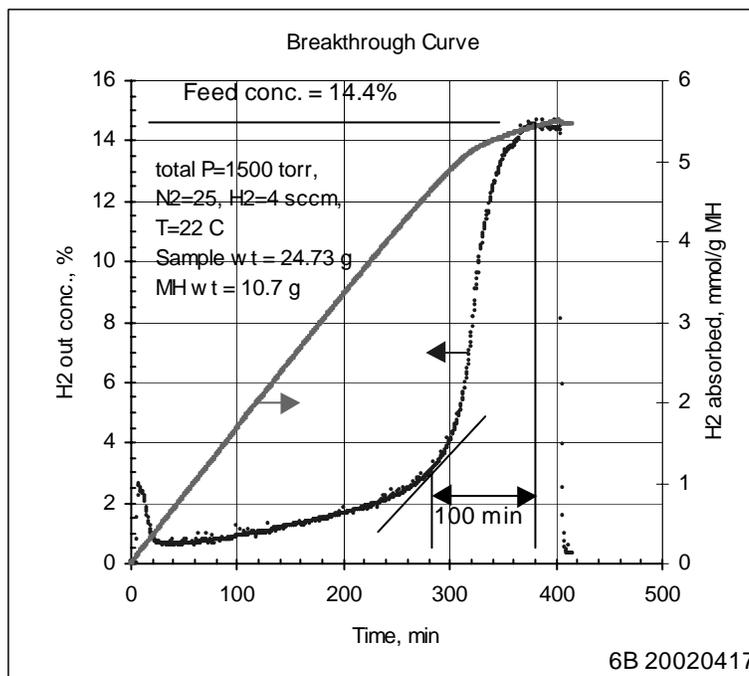


Figure 6. Breakthrough curve and absorption capacity of encapsulated LaN<sub>i4.75</sub>Al<sub>0.25</sub> sample 6B.

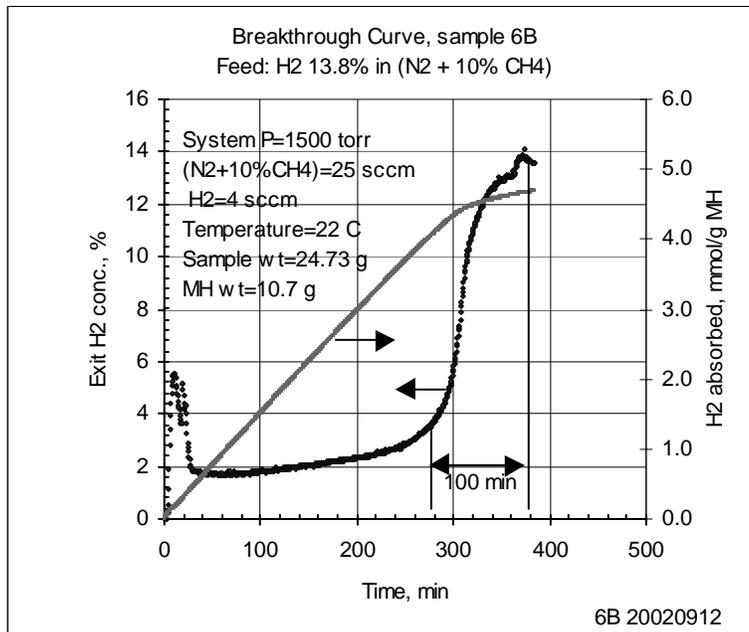


Figure 7. Breakthrough curve and absorption capacity of encapsulated LaN<sub>i4.75</sub>Al<sub>0.25</sub> sample 6B with CH<sub>4</sub> in feed.

### 5.3. Absorption from H<sub>2</sub>, N<sub>2</sub> And CH<sub>4</sub> Mixture

Absorption from mixtures of H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> was conducted the same way as that for H<sub>2</sub> and N<sub>2</sub>, except that the N<sub>2</sub> contained 10% CH<sub>4</sub>. The purpose was to see if CH<sub>4</sub> interfered with the hydrogen absorption. Figure 7 is a breakthrough curve generated with sample 6B. The curve is almost an duplication of that generated without CH<sub>4</sub>. However, there are some slight differences. The hydrogen concentration at the beginning portion of the profile is higher, 2% instead of 1%. The breakthrough capacity is slightly smaller, 4.7 mmol/g instead of 5.5 mmol/g.

### 5.4. Absorption from H<sub>2</sub>, N<sub>2</sub> And CO Mixture

In this set of tests, the nitrogen used to make the feed contained 1% of carbon monoxide. As shown in Figure 8, the presence of CO significantly affected the kinetics and the apparent capacity. The hydrogen broke through the column immediately. The exit hydrogen concentration jumped to 5% right at the start. However, the CO did not completely prevent the packing material from absorbing hydrogen. It took over 400 minutes for the concentration to approach the feed concentration. Since only about half the breakthrough curve was shown, the width of the breakthrough curve was estimated to cover about 800 minutes, 8 times that when CO was

not present. The hydrogen absorbed at 450 minute was only about 3 mmol/g, half of the original. The exposure to CO did not have a permanent effect on the packing material. The material recovered its capacity and kinetics after the hydrogen was desorbed at 120 °C with nitrogen purge.

### 5.5. Absorption By Encapsulated Fluorinated Metal Hydride Powder

Authors in reference 2 reported that LaNi<sub>4.7</sub>Al<sub>0.3</sub> powder treated with fluoride solution gained tolerance to CO. Similar fluorination treatment was given to the LaNi<sub>4.25</sub>Al<sub>0.75</sub> powder before the powder was encapsulated in a silica matrix. The product did improve activation very significantly as discussed above in the

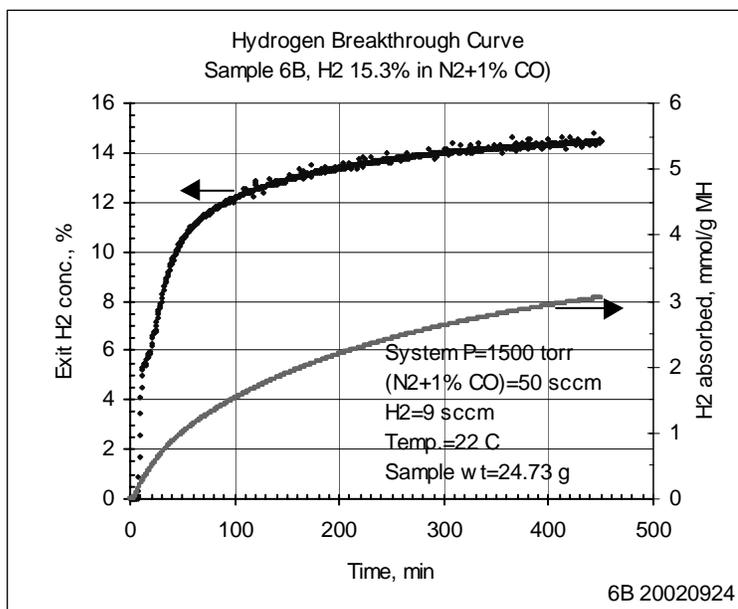


Figure 8. Breakthrough curve and absorption capacity of encapsulated LaNi<sub>4.75</sub>Al<sub>0.25</sub> sample 6B with CO in feed.

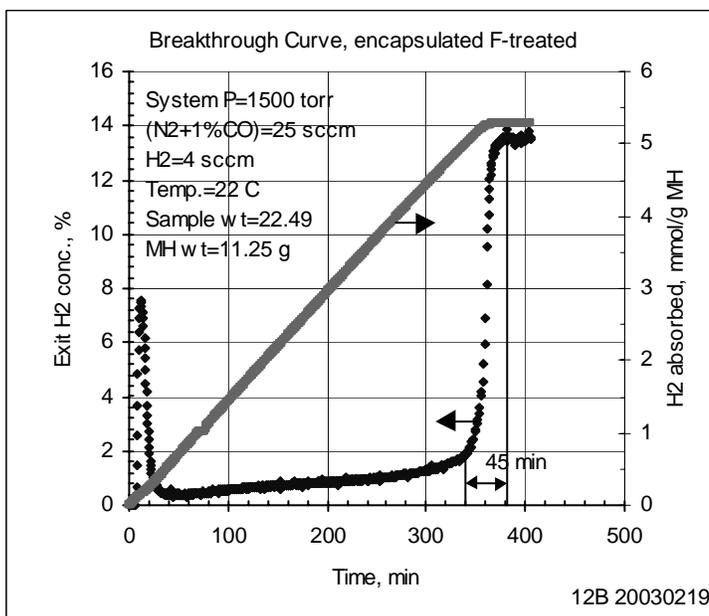


Figure 9. Breakthrough curve of encapsulated fluorinated LaNi<sub>4.75</sub>Al<sub>0.75</sub> with H<sub>2</sub> in N<sub>2</sub> feed.

activation section. In flow through test, the sample showed improved kinetics with a breakthrough curve covered only 45 minutes compared to the 100 minutes of an un-treated sample, when the feed was hydrogen in nitrogen. See Figure 9. However, when 1% CO was added to the feed, both the reaction rate and the capacity fell significantly below that of the untreated but dip coated sample. The capacity was only 0.8 mmol/g. The dip-coated sample had 3 mmol/g. See Figures 10 & 8. The fluorination improved the kinetics but not the tolerance to CO.

### 5.6. Regeneration

After absorption, regeneration was achieved by heating the column to 120 °C with nitrogen purging at 50 sccm.

Exit hydrogen concentration was measured continuously with the TCD. From the concentration profile, the amount of hydrogen recovered and its partial pressure were calculated. Figure 11 shows a typical regeneration result. The partial pressure peaked at 700 torr. The desorbed hydrogen was calculated to be 4 mmol/g accounted for most of the absorbed hydrogen.

### 6. Summary

Two types of silica encapsulated  $\text{LaNi}_{4.75}\text{Al}_{0.25}$  were prepared and tested for hydrogen absorption from streams of gas mixtures. The first type of sample was  $\text{LaNi}_{4.75}\text{Al}_{0.25}$  powder encapsulated in fumed silica and dip coated with TEOS solution. The second type of sample was fluorinated  $\text{LaNi}_{4.75}\text{Al}_{0.25}$  powder encapsulated with fumed silica. Both samples removed hydrogen very well from a nitrogen stream and from a nitrogen plus 10% methane stream. When 1% carbon monoxide was added to the feed, both samples were affected negatively. The capacity of the first type of sample decreased to about 50% and the kinetics reduced to about 1/8. The capacity of the second type of sample decreased to 12% and the kinetics to less than 1/8. Dip coating with TEOS solution appeared to provide more protection for the metal hydride against CO than fluorination. Encapsulated metal hydride is a potential packing material for recovering hydrogen in low concentration gas streams, but its tolerance to reactive impurities needs to be further improved.

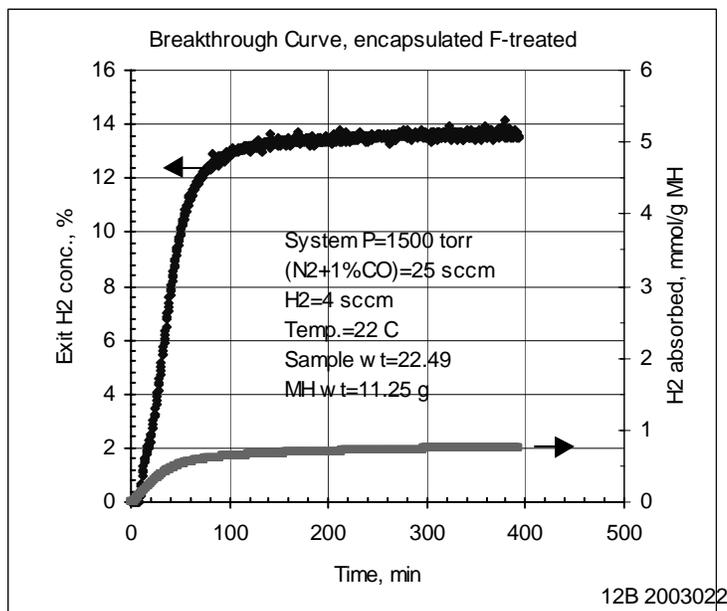


Figure 10. Breakthrough curve of encapsulated fluorinated  $\text{LaNi}_{4.75}\text{Al}_{0.75}$  with CO in feed.

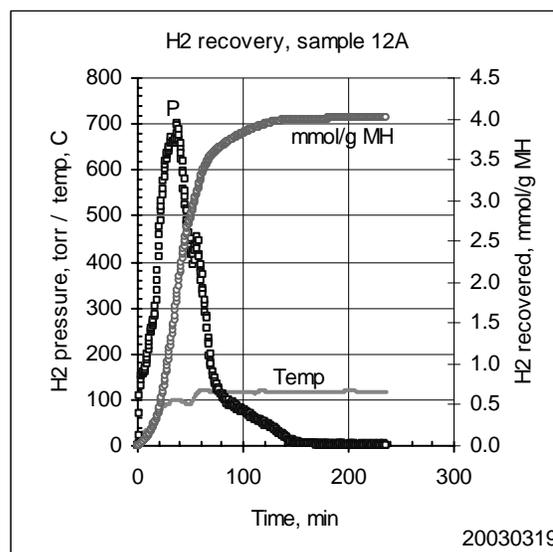


Figure 11. Regeneration with heat and nitrogen purge.

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