



APPLICATION OF FERRIFEROUS HYDROSOL FOR CO₂ CAPTURE

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Introduction. The demand for strategies to reduce global atmospheric concentrations of greenhouse gases is considered one of the main tasks for 21 century. The capture and sequestration of carbon dioxide, the predominant greenhouse gas, is a central strategy of these initiatives. Carbon capture and storage (CCS) schemes embody a group of technologies for the capture of CO₂ from power plants, followed by compression, transport, and permanent storage [1]. The main technologies of CO₂ capture are based on the processes of absorption-desorption in absorbing solutions, membrane separation, adsorption, and mineralization [2, 3, 4]. Technology for the use of absorbent solutions, in particular amines, is common in the industry, while other technologies are in the concept or pilot stages [5]. Carbon capture and utilization (CCU) is an alternative approach to reducing CO₂ emissions [6]. CCU can be realized by chemical fixation through the conversion of CO₂ into fuels, commodity chemicals, construction materials, or mineral carbonates represents another promising alternative for CO₂ capture. Particularly, CO₂ may be considered as feed to produce fuels such as methanol, formic acid, dimethyl carbonate, methyl formate, and higher hydrocarbons, as well as polymeric materials and pharmaceutical chemicals [7].

The carbonate cycle is a novel concept for CCU technology that is based on the adsorption of CO₂ by metal oxides with further transportation and degassing with the regeneration of initial oxide [8]. In metal carbonate decarboxylation, the reaction conditions, especially the nature of the gas atmosphere, play a crucial role in the course of the reaction. If carried out in a reducing atmosphere of hydrogen, the decomposing of carbonate combines with chemical transformations of CO₂ into valuable products. The main advantage of the carbonate method is the possibility of the transformation of carbon dioxide into hydrocarbons using hydrogen [9]. The use of "green" hydrogen in the hydrogenation of carbonates predicts a closed carbon cycle. Iron oxides are a leading candidate for this technology due to the high dissemination and low cost of iron. Iron is an industrial catalyst of Fisher-Tropsch synthesis, a process of obtaining synthetic fuels from synthesis gas [10]. It could be expected, that selection of experimental conditions allows obtaining not only methane and carbon monoxide, as a reaction product, but also higher hydrocarbons. Iron carbonate also can be utilized as inorganic pigment that provides a brown and red-brownish coloring.

As reported in the literature, only Fe²⁺, mainly in the form of FeO, applies to CO₂ capture, while Fe³⁺ is unsuitable for this approach due to its inability to form carbonates. However, FeO is a quasi-stable oxide that disproportionates producing Fe and Fe₃O₄ [11]. Therefore, iron in the form of Fe₃O₄, or a mixture of iron oxides/hydroxides is suitable for large-scale adsorption of CO₂ [12]. Adsorption capacity and kinetics can be increased by the use of a water suspension. The commercial products of

suspension of iron oxides/hydroxides named ferryferrohydrosol (FFH) which is used for purification of waste water, is also predicted to be a perspective adsorbent for CO₂. FFH is a colloidal suspension of two- and three-valence iron hydrated compounds, used as a reagent for wastewater pollutants binding. The method of manufacturing FFH is apparently simple and based on the electrolysis of iron and steel stamping waste. Predicted, that electrolysis of steel leads to a formation of iron-containing oxide-hydroxide nanoparticles that shows a tendency of coagulation into coarse bunches, and the formation of agglomerates with a size of several micrometers. Formed FFH characterizes by enhanced sorption capacity, particularly due to the developed specific surface of iron-containing particles, that can achieve 400 m².

The presented work is dedicated to the assessment of the possibility of capturing CO₂ using the FFH suspension as a perspective product for cleaning concentrated exhaust gases produced by fossil fuel-based enterprises.

Methods. Samples of FFH were provided by the manufacturer, the INECO company (Innovation Ecology), Vilnius, Republic of Lithuania. It was provided 3 samples that contains 40g/l of FFH with 4g/l of NaCl (FFH-NaCl), 30g/l of FFH with 4g/l of Na₂SO₄ (FFH-Na₂SO₄), and 40g/l of FFH with 4g/l of Na₂SO₄ and 2 g/l of a compound (FFH-Na₂SO₄+). Also, commercial magnetite Fe₃O₄ 325 mesh ($\approx 45 \mu\text{m}$) from “Thermo scientific” was used as a sample for comparison. The structure of the samples were characterized by Raman spectroscopy. Raman spectra were performed a HORIBA Jobin-Yvon T64000 spectrometer using exciting Ar-Kr laser radiation at a wavelength of 488 nm and a power of 100 mW. Fourier transform infrared (FTIR) spectra were obtained using a Spectrum-One spectrometer (PerkinElmer). The dynamic light scattering (DLS) measurements were made with a Malvern Zetasizer Nano S, using a 633 nm HeNe laser at 4 mW. Aqueous suspensions of initial FFH, and FFH after CO₂ adsorption were tested in quartz cuvettes having a 10 mm path length. The analysis was operated in backscatter mode at an angle of 173°. Samples were equilibrated at 25 °C for 30 min before measurement. The concentration of FFH in water was 1 mg/ml. The capacity of FFH for CO₂ adsorption was determined using a volumetric method. The flask with a sample was connected to a cuvette filled with dibutylphthalate. The duration of each adsorption experiment was at least 30 minutes.

Results and Discussion. Figure 1 presents FTIR and Raman-spectra of initial FFH samples, commercial Fe₃O₄, and corresponding samples after CO₂ adsorption. A comparison of spectra of initial FFH shows that spectra of FFH-Na₂SO₄+ and FFH-Na₂SO₄ are very similar, while the spectrum of FFH-NaCl shows a noticeable difference. Bands at 340 cm⁻¹, 495 cm⁻¹, and a broad band at 685cm⁻¹ in combination with a band at 1395 cm⁻¹ show, that the main phase of FFH-Na₂SO₄+ and FFH-Na₂SO₄ is maghemite - $\gamma\text{-Fe}_2\text{O}_3$ [13]. The spectra of FFH-NaCl present the same bands combined with two intense bands at 220 cm⁻¹ and 280 cm⁻¹ which are corresponds to hematite - $\alpha\text{-Fe}_2\text{O}_3$ [14]. Raman spectra of magnetite contains a weak band at 540 cm⁻¹ and strong band at 662 cm⁻¹, which are typical bands of magnetite [15].

A comparison of Raman-spectra of initial FFH samples and FFH after CO₂ adsorption shows only a slight decrease of band intensity. The main Raman bands of siderite appear at 190 cm⁻¹, 290 cm⁻¹, and the most intense band at 1100 cm⁻¹ [16]. Therefore, CO₂ adsorption does not lead to the appearance of detectable bands of siderite, which can be caused by a low concentration of formed siderite. Raman spectra of magnetite after CO₂ adsorption are almost identical to the initial Fe₃O₄.

Bands at 570-580 cm⁻¹ in the FTIR spectra correspond to a Fe–O stretching mode of the tetrahedral and octahedral sites of Fe₃O₄ in Fe₃O₄, and FFH samples. Weak band 800 cm⁻¹ can be attributed to a –OH stretching vibration of $\alpha\text{-FeOOH}$ [17, 18]. Bands with low intensity near 1000 cm⁻¹ are the bending vibration of –OH modes in $\gamma\text{-FeOOH}$ and a broad peak at 1100 cm⁻¹ is the bending vibration of OH modes in $\delta\text{-FeOOH}$. Peaks at 1300–1500 cm⁻¹ could be related to the stretching vibration band

of the CO_3 group that mainly arises from the contamination of solutions by atmospheric carbon dioxide [19]. A pronounced band at $\sim 1620\text{--}1630\text{ cm}^{-1}$ is related to the H–O–H bending of water.

Adsorption of CO_2 leads to the appearance of the band at 470 cm^{-1} in FFH- $\text{NaCl}(\text{CO}_2)$ and FFH- $\text{Na}_2\text{SO}_4(\text{CO}_2)$ as well as a new band at 440 cm^{-1} in $\text{Fe}_3\text{O}_4\text{--CO}_2$, which corresponds to metal-oxygen vibration modes of maghemite [20]. The spectra of $\text{Fe}_3\text{O}_4\text{--CO}_2$ contain a doubled band at $520\text{--}750\text{ cm}^{-1}$ which is a result of the combination of Fe–O stretching mode of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. The spectra of $\text{Fe}_3\text{O}_4(\text{CO}_2)$ contain two intense bands at $900\text{--}1100\text{ cm}^{-1}$ that are attributed to surface OH groups in magnetite (960 cm^{-1}) and maghemite (1080 cm^{-1}). There is a significant increase in the intensity of

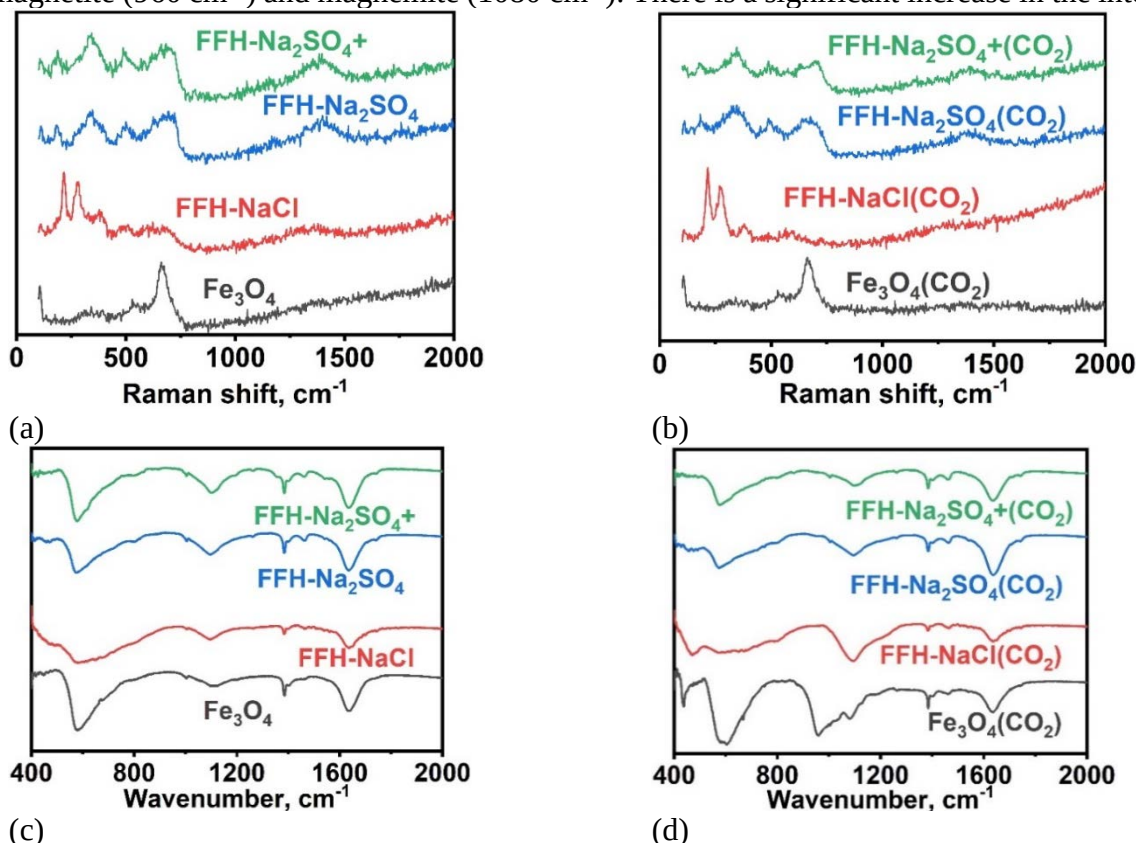


Figure 1. Raman (a) and FTIR (b) spectra of initial FFH samples, commercial Fe_3O_4 , and Raman (c) and FTIR (d) spectra of corresponding samples after CO_2 adsorption.

the band at 1100 cm^{-1} for the FFH- $\text{NaCl}(\text{CO}_2)$ sample in comparison with the initial FFH- NaCl . This result indicates an increase in the content of the phase of $\gamma\text{-FeOOH}$ due to CO_2 adsorption. Adsorption of CO_2 does not lead to significant changes in the FTIR spectra of FFH- $\text{Na}_2\text{SO}_4(\text{CO}_2)$ and of FFH- $\text{Na}_2\text{SO}_4+(\text{CO}_2)$ compared with initial samples.

Table 1. Average particles size of initial FFH samples and FFH after adsorption of CO_2 .

№	Sample	Average particles size, μm
1	FFH- Na_2SO_4+	6.5 ± 0.2
2	FFH- Na_2SO_4	3.4 ± 0.1
3	FFH- NaCl	4.7 ± 0.1
4	FFH- $\text{Na}_2\text{SO}_4+(\text{CO}_2)$	2.8 ± 0.1
5	FFH- $\text{Na}_2\text{SO}_4(\text{CO}_2)$	2.7 ± 0.1
6	FFH- $\text{NaCl}(\text{CO}_2)$	2.6 ± 0.1

Table 1 presents the average particles size of initial FFH samples and FFH samples after CO₂ adsorption determined by DLS. Obtained results show that FFH contains particles of a size of several micrometers. The smaller particles of 2.5 micrometers contain FFH-NaCl, while FFH-Na₂SO₄+ contains the larger particles of 6.5 micrometers. Adsorption of CO₂ decreases the average particle size for all samples to a size close to 2.7 micrometers. This result indicates that the adsorption of CO₂ leads to breaking the bonds in iron-containing particles, probably hydrogen bonds that result in the grinding of the particles agglomerates to smaller initial particles. Therefore, analysis shows, that FFH contains a suspension of iron-containing particles with a size of several micrometers which are a mix of oxides and hydroxides of Fe²⁺ and Fe³⁺. The main crystalline phases of these particles are maghemite, hematite, and magnetite with a significant content of their hydrated forms. It can be speculated, that the main amount of CO₂ adsorbs by Fe in amorphous forms, which are the major phase of Fe in FFH. Adsorption of CO₂ has a limited effect on the transformation of crystalline phases, which consists in the transition of the magnetite phase to maghemite. While the amorphous phase of particles adsorbs CO₂ by surface OH-groups and oxides forming nanostructures containing carbonates and hydroxycarbonates that aggregate into particles with sizes near 2.5-3 micrometers.

Table 2 presents experimental results of the adsorption of CO₂ by FFH samples. At 20 °C FFH adsorbs 3-4.5 liters or 6-8.5 g of CO₂. The ultimate amount of adsorbed CO₂ by iron oxide/hydroxide systems can be calculated according to the ratio, where 1 mole of Fe adsorbs 1 mole of CO₂. This proportion follows from the equation FeO+CO₂=FeCO₃. Therefore, 1 liter of FFH, which contains 40 g of Fe, can adsorb 31.4 g or 16 liters of CO₂. Adsorption of CO₂ by water is negligible due to the influence of electrolyte and solid particles, which dramatically reduce the adsorption capacity of the water. Therefore, according to this approach, the adsorption capacity of FFH samples is 8.5-14.5% of the theoretical value. This indicates that only a limited amount of iron compounds adsorbs CO₂. The adsorption capacity determined experimentally is lower than the theoretic value, which can be caused by the inaccessibility of the inner part of particles to the CO₂ at 20 °C. The high content of Fe³⁺ is another reason of the depressed capability of FFH towards the adsorption of CO₂. Adsorption of CO₂ by magnetite is negligible, that is a consequence of a very low specific surface due to large particles size.

Table 2. The density of FFH samples, the amount of adsorbed CO₂ by FFH samples at 20° C, and the amount of adsorbed CO₂ relative to the theoretic value obtained from the proportion of (1 mole CO₂)/(1 mole FeO).

Sample	Density, g/cm ³	liter(CO ₂)/liter(FFH)	g(CO ₂)/kg(FFH)	g(CO ₂)/g(Fe)	% from theory
FFH-Na ₂ SO ₄ +	1.06	3.1	5.8	0.15	8.5
FFH-Na ₂ SO ₄	1.04	3.9	7.4	0.26	14.5
FFH-NaCl	1.05	4.3	8	0.21	12
*Fe ₃ O ₄	-	<0.01	<0.1	<0.001	<0.001

* Experiment of CO₂ adsorption by Fe₃O₄ was provided using a suspension of 40g Fe₃O₄ and 4g NaCl in 1 liter of water

Comparison of data presented in Table 1 and Table 2 shows, that amount of adsorbed CO₂ increases with a decrease of particles size of FFH. This result indicates that the influence of particles

size on the adsorption capacity is very significant. Therefore, a strategy for the creation of a highly effective FFH is not only to obtain a FFH with a high content of Fe^{2+} but also with a small size of iron-containing particles. Also, it can be concluded that the main role of electrolytes is the determination of particles size of FFH, and the influence of various electrolytes on differences in phase composition, the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$, and, as a consequence, the adsorption capacity is negligible.

The alternative approach, which is based on the study of model systems of iron oxides, shows that at room temperature is mainly observed physical adsorption of CO_2 on all types of iron oxides. It was shown, that the degree of surface hydroxylation plays a decisive role in the adsorption of CO_2 on the surface of iron oxides, which leads to the formation of adsorbate forms identified as surface bicarbonates. Adsorbed CO_2 over a long period of time can transform into a chemisorbed form with the formation of carbonates and bicarbonates. However, such a process occurs only in the presence of Fe^{2+} [21, 22, 23]. According to this, a developed surface of iron oxides is required for an increase in the absorption capacity. The maximum amount of $3.01 \cdot 10^{-3} \text{ gCO}_2/\text{g}$ of absorbed CO_2 was observed for Fe_2O_3 . The adsorption of CO_2 by a biochar/Fe oxyhydroxide sorbent of $0.16 \text{ gCO}_2/\text{g}$ at 25°C was achieved [21].

Following this approach obtained values of adsorbed CO_2 by FFH allow the determination of the specific surface area (SSA) of iron particles which can be calculated using:

$$S = q \cdot \sigma_0 \cdot N_A$$

where, q is the adsorption capacity of CO_2 (mol/g), σ_0 is the area claimed by an adsorbed molecule of CO_2 ($0.109 \cdot 10^{-18} \text{ m}^2$), and N_A is Avogadro's number ($6.022 \cdot 10^{23} \text{ mol}^{-1}$). The obtained result of the SSA of iron in FFH gives $220\text{-}390 \text{ m}^2/\text{g}$. Comparing the values of SSA and particles size obtained by DLS confirms that the iron-containing oxide particles in the samples are porous agglomerates of smaller, mostly amorphous nanoparticles with a highly developed surface.

Conclusions. The possibility of applying FFH for the absorption of CO_2 from concentrated exhaust gases was demonstrated. It was shown, that the structure of FFH is a suspension of iron-containing nanoparticles which are a mix of oxides and hydroxides of Fe^{2+} and Fe^{3+} . These nanoparticles are agglomerated in larger particles with a size of several micrometers. The main crystalline phases of these particles are maghemite, hematite, and magnetite with significant content in their hydrated forms. FFH samples have a developed surface in the range of $200\text{-}400 \text{ m}^2/\text{g}$. The absorption capacity for CO_2 of $0.26 \text{ g(CO}_2)/\text{g(Fe)}$ at room temperature was shown. A high absorption capacity of FFH can be associated with a highly developed surface area of the samples and a high degree of surface hydroxylation. Therefore, the use of FFH to absorption of CO_2 from concentrated exhaust gases has significant advantages over solid sorbents.

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