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ORIGINAL ARTICLE

CO_2 Adsorption on Zeolite and Fe-MOF for Carbon Capture and Storage (CCS)

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ABSTRACT – This research focused on the development of suitable materials for capturing and storing CO_2 (CCS). Ferum-metal organic framework (Fe-MOF) and zeolite were prepared as adsorbents for the CO_2 adsorption process. These adsorbents were characterised by employing X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) analysers. The adsorptive capacity of CO_2 was conducted in an assembled facility containing of a metallic tubular container set up with a pure CO_2 gas stream from a cylinder-shaped tank. The performance of these two adsorbents was investigated using two different parameters which are operating pressure and dosage of adsorbents. The exit concentration of CO_2 was analyzed periodically using gas chromatography. Based on the FTIR and XRD studies, the findings suggest that the zeolite and Fe-MOF were successfully formed. The optimal adsorption conditions obtained for both adsorbents were 0.3 g of adsorbent dose and 1 bar of operating pressure. In conclusion, zeolite exhibits better performance as a CO_2 adsorber due to its higher adsorption capacity than Fe-MOF.

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INTRODUCTION

CO_2 is an important heat-trapping (greenhouse) gas, which is released through human activities such as deforestation and burning of fossil fuels, as well as natural processes such as respiration and volcanic eruptions [1]. In order to reduce the CO_2 level released to the environment, carbon capture and storage (CCS) is introduced. This technology involves collecting up to 90 % of CO_2 discharged from industrial and energy-related sources before or after ignition, compressing and splitting, transporting to a sequester location and injecting it deep underground in healthy geological formations, and finally disposing it using a process that will completely eliminate it from the atmosphere [2].

Adsorption is one of the techniques for the separation and capturing gas. This method is considered an appropriate option for capturing CO_2. It offers benefits such as lower CO_2 capture costs, higher CO_2 transport ability, lesser regenerative energy requirements, rapid reaction rates and minimal pressure reduction. Because of its lower energy demands and simpler operating conditions, the use of adsorbents to capture CO_2 has emerged as aviable alternative [3].

In the present study, metal organic frameworks (MOFs) and zeolites were selected and applied as adsorbents in the adsorptive process to capture CO_2. MOFs exhibit outstanding substances for CO_2 sequester, and also they are suitable in the elimination of CO_2 from flue gas stacks [4]. These MOFs are composed of organic linkers connecting metal ion clusters such as the one used in this study, ferric ion, both of which can be modified for easy tuneable of the structures of their pores, exterior functions and other qualities by comparing them to the other porous materials, making them suitable for a variety of unique and precise applications as porous materials [5]. In the meanwhile, zeolites are applied in gas separation, ion exchange and as a catalyst due to their excellent chemical and thermal firmness as well as their enormous capacity to split mixtures of molecules based on preferential adsorption. Furthermore, because of their small and flexible microporosity, zeolites demonstrate shape-selective molecular sieving [6]. A large number of MOFs and zeolites studies have examined CO_2 adsorption isotherms at high pressure condition, unfortunately, creating the research gap on the data development for low pressure system. Hence, further studies are needed to fully characterise these materials for their specific application.

The objective of this work is to advance the understanding of the performance of materials for CO_2 capture and separation at low pressure process conditions. Therefore, in this study, Fe-metal organic frameworks (MOF) was employed as the sorbent material and compared with the benchmark zeolite over the same pressure and dosage range.

MATERIALS & METHODS

Materials

In the preparation of adsorbents, the materials and chemicals used included coal, sodium hydroxide (NaOH), sodium aluminate ($NaAlO_2$), 95 % ethanol (C_2H_5OH), 98.5 % ferric nitrate (III) nanohydrate ($Fe(NO_3)_3.9H_2O$), 98 % benzene-1,3,5-tricarboxylic acid ($C_9H_6O_6$) and deionized water. All materials were supplied from Capital Eng Resource Sdn Bhd and directly applied in the experiment without any further purification.

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Preparation of zeolite

The preparation of zeolite was conducted following the procedure by [7]. The coal was crushed into small kernels by a ball crusher with a rotation speed of 400 rpm. Then it went through 200 mesh screens before charred at 850 °C for 2 hours in a muffle kiln to eliminate carbon. Subsequently, 4.0 g of treated coal gangue, 7.0 g of NaOH and 0.574 g of $NaAlO_2$ were mixed with 64 mL of deionized water and aged at 25 °C for 2 hours. The solution was moved to a Teflon-coated stainless steel reactor and reacted hydro-thermally at 90 °C for 3 hours. After the process was completed, the product was gathered by the Buchner funnel and rinsed with deionized water 3 times and kept in the oven to dry the product.

Preparation of Fe-MOF

Fe-MOF was prepared using a simple low temperature synthesis process from [8]. The synthesis was started by mixing 1,3,5-benzenetricarboxylic acid ($C_9H_6O_6$) and ferric nitrate (III) nanohydrate ($Fe(NO_3)_3.9H_2O$) at ambient pressure. $Fe(NO_3)_3.9H_2O$ (4.04g), $C_9H_6O_6$ (1.89 g) and deionised water (6 mL) were blended and charged into a 25 mL beaker set up with a magnetic stirrer and a reflux condenser, and held at 120 ºC and 300 rpm for 3 hours. The product was rinsed three times using 350 mL deionized water and 350 mL ethanol in a solvent extraction process at 70 ºC for 24 hours, then dried out in a vacuum desiccator at 150 ºC for 10 hours.

Characterisation of adsorbents

Fourier Transform Infrared Spectroscopy (FTIR) (Model Perkin Elmer FTIR-2000, US) was employed to investigate and define the chemical bonds and functional groups of the adsorbents. The spectrums were recorded starting from 4000-400 cm^{-1}. Powder X-ray diffraction (XRD) data from the two adsorbents were gathered by Geigerflex (Rigaku, Inc) diffractometer employing Cu Kα radiation (0.154 nm) with a 5.0 to 60.0 scan (parameters: voltage (30 kV), current (40 mA) and step size (0.050).

CO_2 adsorption process

The adsorptive capacity of CO_2 process took place in a stationary-bed stainless steel reactor. The experiments were first carried out without resorting to adsorbents to obtain a pure concentration of CO_2. Afterwards, a certain amount of adosrbent was placed in the reactor and cotton was added on both ends of the reactor. Temperature and working pressure were set. Once the CO_2 run out and achieved the designated pressure, all incharge and discharge valves were fastened and set for the adsorption process. The CO_2 gas specimen was collected in a sampling bag. Afterwards, the sample was injected in gas chromatography to detect the gas concentration. Subsequently, the quantity of CO_2 sorbed at any interval time was calculated using Equation 1 below:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{1}$$

where q_t represents the quantity of CO_2 adsorbed per unit adsorbent mass (mg/g). C_o and C_t represent the initial CO_2 concentration (mg/L) and the CO_2 concentration (mg/L) at time t, respectively, while m and V denote the mass of the adsorbent (g) and the volume of the reactor (L).

EXPERIMENTAL RESULTS

Characterisation of adsorbents

Adsorbent characterisation is crucial for identifying the physical and chemical qualities and features that have a direct impact on the capability of adsorbents in the adsorptive capacity CO_2.

Fourier Transform Infrared Analysis (FTIR)

FTIR study was performed to investigate the type of functional groups of adsorbent exteriors and also to confirm the emergence of prepared adsorbents. The FTIR spectra (4000-500 cm^{-1}) from the synthesized zeolite and Fe-MOF were presented in Figure 1. Concerning the bands of the FTIR spectra in Figure 1, which is attributed to zeolite as an adsorbent for CO_2 adsorption, the wide-ranging bands were discovered respectively in the region range of 2848.82 cm^{-1}, which are associated to the tensile bond of OH. As can be seen in Figure 1, peaks were observed in regions of 1100.67 cm^{-1}, which are associated with CO tensile bonding. In addition, the significant peaks that apppear at 2147-1968 cm^{-1} can be assigned to the C=C stretch. FTIR spectra for zeolite also showed a characteristics of Si-O stretching peak at 979 cm^{-1}. It is important to mention that the wave number associated with the Si-O bond to prove that the prepared adsorbent in this work is zeolite.

With regard to the bands of the FTIR spectrums in Figure 1, which connected to Fe-MOF as adsorbent for CO_2 adsorption, the peak at 2289.31 cm^{-1} attributed to C-O bond of carboxylate groups, whereas the bands at 1214.93 and 1130.08 cm^{-1} are respectively associated to asymmetric and symmetric vibrational peaks characteristic of -O-C-O- group. The FTIR results of Fe-MOF shows a significant peak at 2963-2865 cm^{-1} which is attributable to the (OH) stretching.

Moreover, the stretch vibration of C=O groups is appeared at 1364 cm^{-1}. Therefore, the presence of these functional groups are responsible for its adsorptive property which are responsible for CO_2 adsorption process.

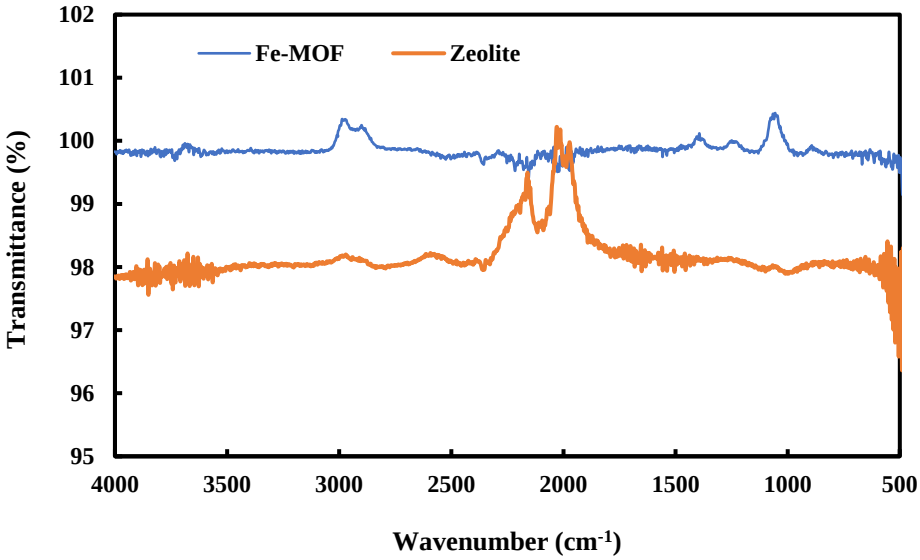
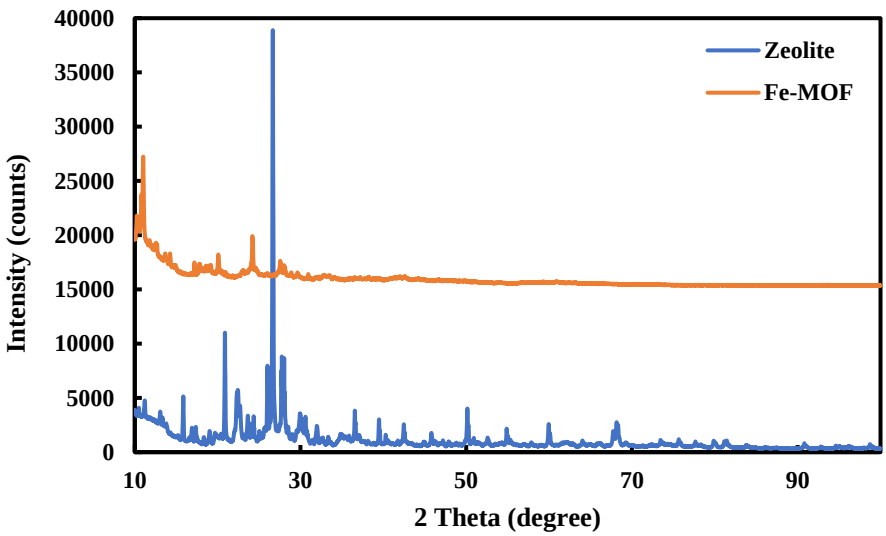


Figure 1. FTIR spectra of zeolite and Fe-MOF adsorbents.

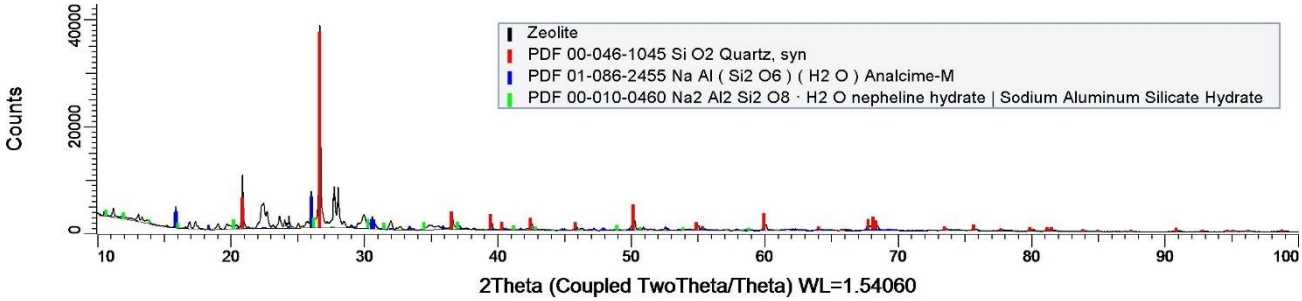
X-Ray Diffraction Analysis (XRD)

The zeolite and Fe-MOF XRD diagrams are illustrated in Figure 2. According to the XRD diagram with the chemical components shown in Figures 2(a) and (b) for zeolite, the highest band intensity was detected at 26.89°, which refers to a high degree of crystallinity. Some low intense weak peaks are observed in Figure 2(b), which indicates the presence of SiO_2, $NaAlSi_2O_6{\bullet}H_2O$ (analcime-M) and $Na_2Al_2Si_2O_8{\bullet}H_2O$ (sodium aluminum silicate hydrate) phases. Previous works suggest that high temperature mayproduce SiO_2 during the formation of zeolite [9]. The 2θ diffraction points of 16.0°, 21.1°, 26.81°, 27.88° and 50.18° are associated with the typical zeolite structure, which confirms its successful formation.

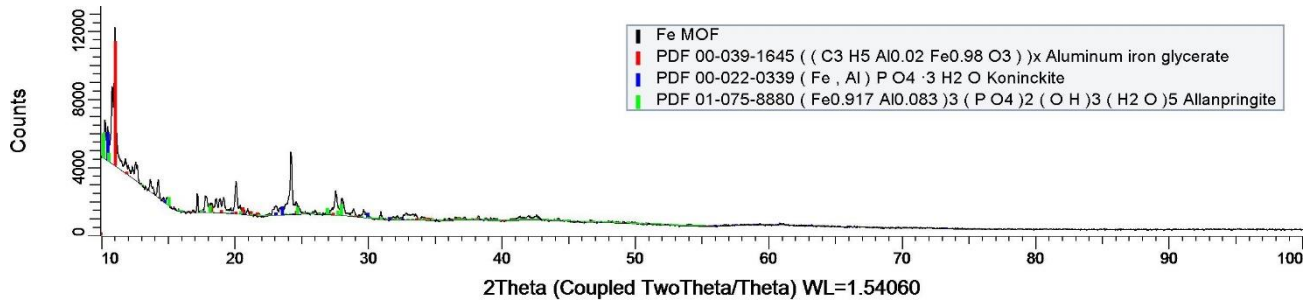
As per Figures 2(a) and (c), the configuration of Fe-MOF has been assigned to specific phase peaks. Across the spectrum, the primary diffraction bands were observed at 11.02°, 20.07°, and 24.19°. The presence of $C_3H_5Al_{0.02}Fe_{0.98}O_3$, $FeAlPO_4{\bullet}3H_2O$ and $(Fe_{0.917}Al_{0.083})_3(PO_4)_2(OH)_3(H_2O)_5$ components confirm the successful development of Fe-MOF.



(a)



(b)



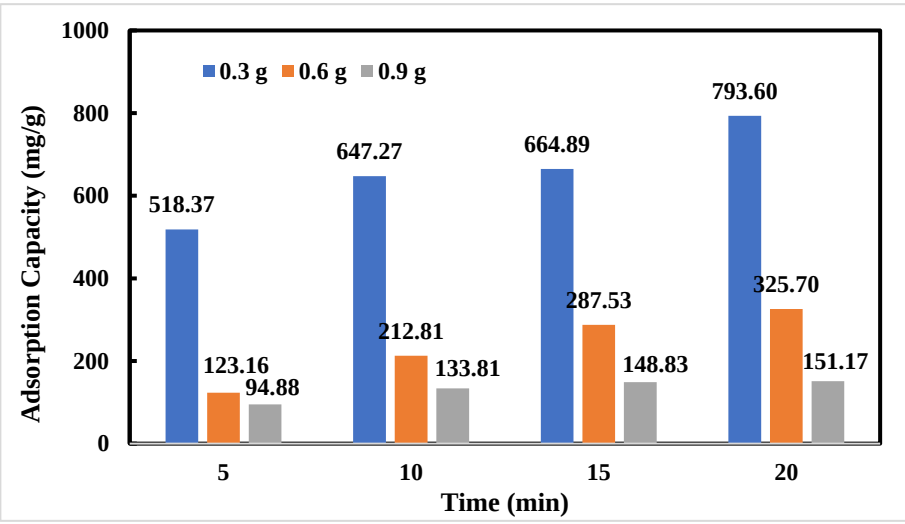
(c)

Figure 2. XRD spectra of (a) zeolite and Fe-MOF, (b) chemical compositions of zeolite, and (c) chemical compositions of Fe-MOF

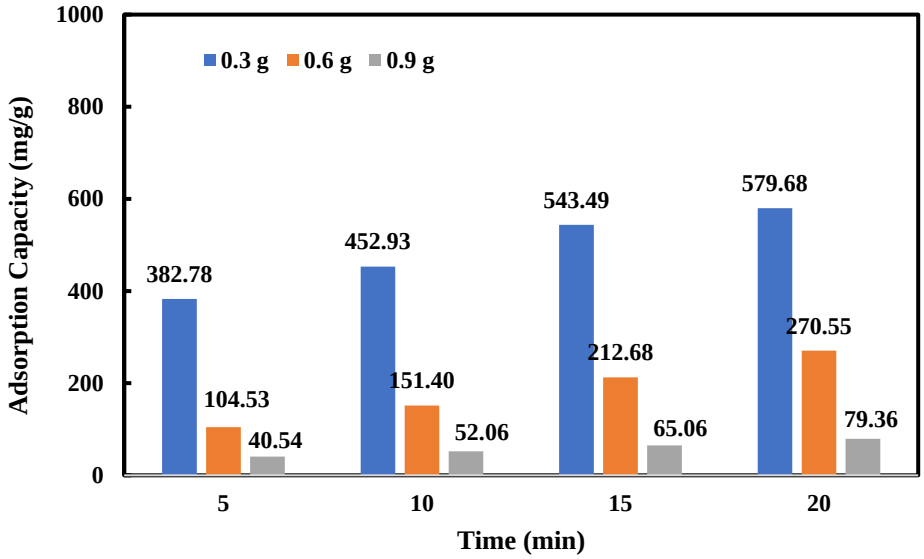
Impact of adsorbent dosage on the adsorptive capacity of CO_2

To examine the impact of the adsorbent dose on the adsorptive capacity of CO_2, a series of adsorption experiments were carried out with doses ranging from 0.3-0.9 g. Effect of modifying the quantity of dose adsorbents on CO_2 adsorption was investigated at constant temperature of 27 °C and pressure of 1 bar.

The results show that as the adsorbent dose rises, the adsorption capacity of both adsorbents declines, as shown in Figures 3(a) and (b). When the amount of adsorbents increases, the overall surface area accessible for CO_2 adsorption decreases due to adsorption site overlapping or aggregation [10]. Additionally, 0.3 g of adsorbent dosage was found as an optimum amount for both adsorbents where zeolite reached the highest CO_2 adsorbed amount, q_t = 793.60 mg/g, compared to Fe-MOF, q_t = 579.68 mg/g. A comparison of the adsorption capacities of the Fe-MOF and the zeolite is shown in Figure 3. The slightly different CO_2 adsorption capability might be due to the different structural properties for both adsorbents as shown in Figures 1 and 2. The major cation of zeolite is Na and this major cation appears to play a main role in the adsorption of CO_2. Also, sodium appears to be the favourable cation for the adsorption of CO_2 [11]. It is noted that this adsorption process occurred at low pressure condition. For zeolite, the CO_2 reaches saturation at relatively low pressure range compared to Fe-MOF and these findings are confirmed from the previous study [12].



(a)



(b)

Figure 3. Impact of adsorbent dose for (a) zeolite and (b) Fe-MOF on CO_2 adsorption capacity.

Impact of operating pressure on the adsorptive capacity of CO_2.

Figure 4 shows the influence of pressure on the adsorptive capacity of CO_2 for zeolite and Fe-MOF. The pressure was varied from 0.2 to 1 bar with the constant operating temperature at 27 ºC with 0.3 g of the amount of adsorbent dosage.

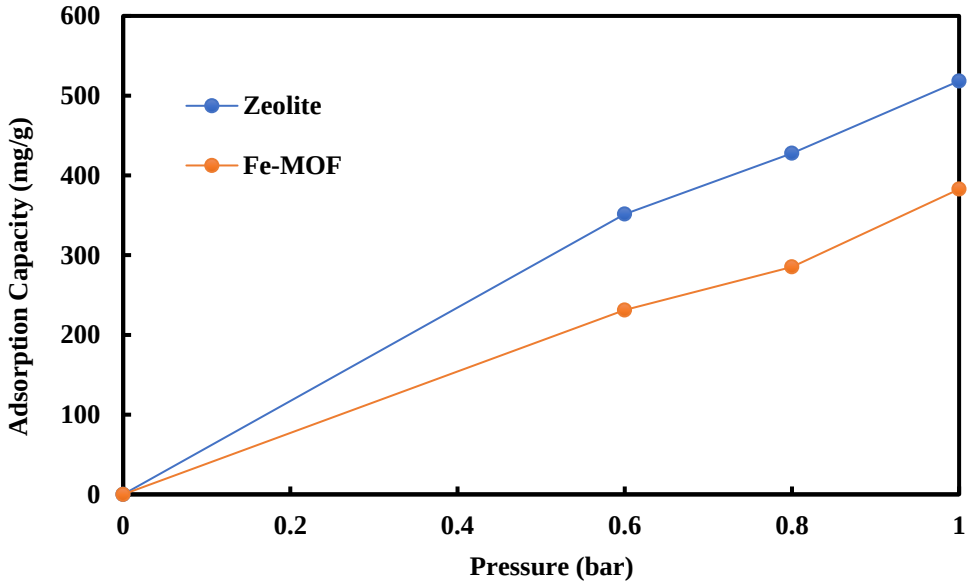


Figure 4. Influence of operating pressure on the adsorptive capacity of CO_2.

The increase in pressure contributes a direct impact on the adsorption ability where the maximum CO_2 adsorption capacity was achieved at a pressure of 1 bar for both adsorbents, as illustrated in Figure 4. Zeolite shows the highest CO_2 adsorption capacity with 518.37 mg/g, whereby only 328.78 mg/g for Fe-MOF at 1 bar pressure, representing ca. 57 % increase in adsorption capacity. It can be seen that the amount of CO_2 adsorbed on the adsorbent increases rapidly with the increase in pressure over the low pressure range as shown in Figure 4. The CO_2 uptake for Fe-MOF was lower than zeolite (at lower pressure). But at higher pressure (up to 35 bar), the CO_2 uptake for Fe-MOF was higher than that of the zeolite [11]. The low pressure range is more suitable for zeolite which demonstrated higher tendency of attracting the quadrupole structure of CO_2. However, when the operating pressure is above 500-1000 kPa, zeolite shows lower uptake capacities than MOFs due to lower pore volumes. Therefore, the capacity becomes limiting for high-pressure operations [13].

CONCLUSIONS

The CO_2 adsorption experiments were conducted at different dosages and pressure. From this study, the findings demonstrated that the CO_2 adsorption capacity increases with increasing pressure and decreases with increasing dosage. Among the two adsorbents tested, zeolite offers higher adsorption capacity than Fe-MOF at dosages ranging from 0.3 to 0.9 g and pressures up to 1 bar. The results from this study provide fundamental knowledge for the treatment of flue gas containing CO_2 by solid adsorption process.

ACKNOWLEDGEMENTS

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