# Geothermal silica waste as raw material for preparing CO<sub>2</sub> sorbents

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#### Introduction

 $CO_2$  management has been promoted and proposed in recent years due to the negative effects of increasing  $CO_2$  emissions. That is why developing and deploying carbon capture, utilization and storage (CCUS) technologies has been widely recognized as a strong alternative for decarbonizing industry and promoting net  $CO_2$  removal from the atmosphere (Zhang et al. 2022). One critical point to implementing CCUS technologies is the  $CO_2$  sorbent material, which must have high  $CO_2$  sorption capacity and stability under different gas stream conditions, good kinetics, and be able to regenerate at a low cost. It is thus that under the circular economy approach, the use of industrial waste as raw material for preparing  $CO_2$  sorbent materials is an attractive topic due to the advantages it offers, such as availability, abundance, low cost, high reactivity, and a complex matrix where the presence of different elements can favor capture or regeneration processes.

Geothermal silica waste is a by-product of geothermal power plants where the water and steam extracted from the underground are used to generate electricity. It has been reported that approximately 50,000 tons of this type of waste are disposed of annually with no planned application (Gomez-Zamorano et al. 2016). Geothermal silica waste mainly comprises amorphous silica (>80%) with low sodium and potassium chloride. This waste could be used in construction as a silica source for alkaline silicate solutions, alkali-activated binders, geopolymers, and Portland cement replacement (Estévez-Jácome et al. 2022). Considering this wide range of potential uses, in this work, geothermal silica waste was used to prepare CO<sub>2</sub> sorbents, lithium silicate, and SiO<sub>2</sub>-amine materials, and the CO<sub>2</sub> capture capacity, kinetic behavior and regeneration properties were evaluated.

## **Experimental**

Silica waste was obtained from two Mexican geothermal power plants and characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD),  $N_2$  adsorption-desorption, and scanning electron microscopy (SEM). Two sorbents, alkaline silicate and SiO<sub>2</sub>-amine materials, were prepared from geothermal silica waste. Alkaline silicate was prepared using the solid-state reaction method from silica waste and  $Li_2CO_3$ . At the same time, SiO<sub>2</sub>-amine adsorbents were obtained by functionalizing silica waste with PEI (polyethyleneimine) and TEPA (tetraethylenepentamine) using the wet impregnation method. The  $CO_2$  capture behavior of the two types of materials was evaluated by thermogravimetric analysis (TG) using  $CO_2$  concentrations between 20 and 5vol% at different temperatures. Finally, the regeneration capacity was evaluated through consecutive adsorption-desorption cycles.

## Results and discussion

According to the XRF results (Table 1), the main component of the geothermal silica waste is silicon (92 wt% as SiO<sub>2</sub>), and DRX analysis confirms the silica's amorphous nature.

Table 1. Chemical composition of geothermal silica waste by X-ray fluorescence (wt%)

$SiO_2$	Na <sub>2</sub> O	$K_2O$	CaO	$Fe_2O_3$	MgO	MnO	$TiO_2$	$LOI^a$
92.088	0.98	0.208	0.529	0.069	0.055	0.024	0.047	6.00

<sup>&</sup>lt;sup>a</sup> LOI: loss on ignition

The  $\text{Li}_4\text{SiO}_4$  formation was corroborated by XRD analysis (Figure 1), and the specific surface area was less than 1 m²/g. The CO<sub>2</sub> capture tests were performed at temperatures between 550 and 6500 °C and CO<sub>2</sub> concentrations between 5 and 20 vol%. The CO<sub>2</sub> capture over time shows an exponential behavior at all temperatures and CO<sub>2</sub> concentrations. As the CO<sub>2</sub> concentration decreases, the reaction slows down, and the capture capacity also decreases. Li<sub>4</sub>SiO<sub>4</sub> reached the maximum CO<sub>2</sub> capture of 143 mg<sub>CO2</sub>/g<sub>material</sub> at 600 °C and 20 vol% CO<sub>2</sub>. Lithium silicate presents good stability over 20 cycles of adsorption-desorption.

For SiO<sub>2</sub>-amine materials, the impregnation of PEI and TEPA molecules on the silica waste surface was corroborated by FTIR and TG analysis. The CO<sub>2</sub> adsorption in the SiO<sub>2</sub>-PEI and SiO<sub>2</sub>-TEPA materials was studied by isothermal thermogravimetric experiments. For SiO<sub>2</sub>-amine materials, the impregnation of PEI and TEPA

molecules on the silica waste surface was corroborated by FTIR and TG analysis. The  $CO_2$  adsorption in the  $SiO_2$ –PEI and  $SiO_2$ -TEPA materials was studied by isothermal thermogravimetric experiments.

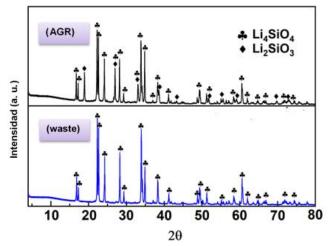


Figure 1. DRX patterns of the lithium silicates prepared with geothermal silica waste and analytical grade reagents (AGR).

The isotherms show an exponential behavior; at the beginning, the adsorption occurs very fast, and as time passes, this rate decreases. The rate of  $CO_2$  adsorption diminishes because the active sites are occupied as the adsorption occurs. The effect of temperature on the  $CO_2$  adsorption rate was assessed with 5 vol% of  $CO_2$  (Figure 2).  $CO_2$  adsorption increases as the temperature increases (30–70 °C). Thus, the best  $CO_2$  capture was achieved at 70 °C (28  $mg_{CO2}/g_{mat}$ ), and higher temperatures did not cause an increase in adsorption.

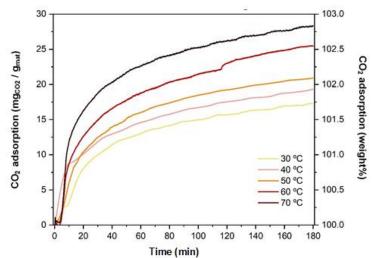


Figure 2. Temperature effect on the CO<sub>2</sub> adsorption capacity of the SiO<sub>2</sub>–PEI adsorbent with 5 vol% CO<sub>2</sub> for 180 min.

#### **Conclusions**

Geothermal silica waste was successfully used as a precursor of two types of  $CO_2$  adsorbents, alkaline silicates and  $SiO_2$ -amine materials, for high and low temperatures, respectively. According to the results, lithium silicate achieved a  $CO_2$  capture capacity of 143 mg $CO_2$ /gmaterial and showed good stability over 30 cycles of sorption-desorption. The  $SiO_2$ -amine materials demonstrate good  $CO_2$  adsorption with low  $CO_2$  concentrations and temperatures up to 70 °C, and regeneration was possible by increasing the temperature to 100°C.

### References

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