

CO₂ CAPTURE AT HIGH TEMPERATURE USING SLAG – DERIVED LITHIUM SILICATES

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Introduction

Alkali-based ceramics such as Li₄SiO₄ are particularly promising for CO₂ capture due to their high CO₂ uptake, sorption/desorption stability and rapid sorption-desorption kinetics. The use of waste materials such as fly ash and rice husk ash as precursors for CO₂ sorbents is receiving increasing interest due to their availability and low cost. Lithium and sodium silicates from fly ashes have been studied as CO₂ sorbents and promising results at low temperatures (around 600 and 650°C) was found.^{1,2} Nevertheless, the use of slags has not been studied into depth for this application.

Therefore, the aim of this work is to prepare Li₄SiO₄-based sorbents from iron and steel slags, as the source of SiO₂, for CO₂ capture.

Experimental

Two slag samples, named S-1 and S-2, were received from different iron and steel Mexican industries. S-1 is a blast furnace slag while S-2 is an electric induction furnace slag. The chemical composition, as determined by X-ray fluorescence was previously reported.³

Table 1. Chemical composition of slags by X-ray fluorescence

	P ₂ O ₅	SiO ₂	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O
S-1	0.03	39.69	1.51	0.94	11.39	1.38	10.15	32.99	0.17	0.56
S-2	0.04	53.75	0.18	13.01	16.90	6.77	3.41	2.65	1.46	2.14

The slag-derived lithium silicates were prepared by mixing Li₂CO₃ (Meyer) with iron and steel slags (S-1 and S-2) in the molar ratio of Li₂CO₃:SiO₂ of 2:1. The mixed powders were calcined at 850°C for 8 h. After calcination, the materials were homogenised and the mineralogical phases were analysed by X-ray diffraction in an Empyrean diffractometer with CuKα radiation and PIXcel3D detector. The samples were measured over a 2-theta angle of 5–70° in steps of 0.003° and 40 s integration time.

The phases were identified using the Inorganic Crystal Structure Database (ICSD). The nitrogen adsorption–desorption isotherm of the materials was also obtained on a Bel-Japan Minisorp II instrument at 77 K using a multipoint technique (N₂ from Praxair, grade 4.8). Prior to analysis, the sample was degassed at room temperature for 12 h. The surface area was determined using the Brunauer–Emmett–Teller (BET) method.

The CO₂ capture of the slags-derived lithium silicates was evaluated by temperature programmed carbonation (TPC) and temperature programmed decarbonation (TPDC) using a Belcat-B from Bel Japan equipped with a TCD detector. Approximately 100 mg of sorbents were kept in contact with a gas stream containing a 5% CO₂ mol fraction (Praxair, CO₂:He = 5:95, mol/mol, certificated standard), and were subject to a 5°C/min temperature ramp. Additionally, temperature programmed desorption (TPD) of CO₂ at different temperatures (500-650°C) was performed. Samples (50 mg) were previously treated in flowing He (Praxair, UHP) at 200°C for 1 h to clean the surface, and then CO₂ was adsorbed for 1 h at desired temperature. After purging CO₂ with He for 10 min, the CO₂-TPD were carried out in He flow (30 mL/min) by a dynamic heating process up to 850°C at a rate of 10°C/min.

Results and Discussion

Figure 1 shows the XRD patterns of iron and steel slag (S-1 and S-2) and slag- derived lithium silicates samples.

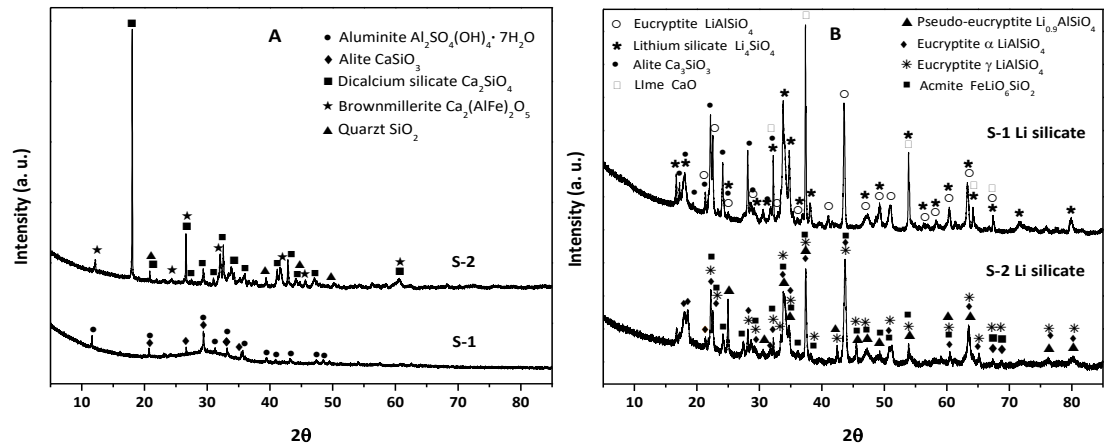


Figure 1: Powder X-ray diffractograms of metallurgical slag (a) and slag –derived lithium silicates (b)

The XRD patterns of S-1 shows that the main phases are aluminite and alite, while in S-2 are dicalcium silicate and brownmillerite, these differences correspond to the process in which the slags were generated. After synthesis of lithium silicates (Figure 1B), the formation of Li_4SiO_4 as well as other lithium and calcium compounds ($LiAlSiO_4$, CaO and Ca_2SiO_2) were observed in the modified S-1. In the S-2 derived product, Li_4SiO_4 was not identified, but the phase of $LiAlSiO_4$ can be fitted to the PDF files. The textural properties of both slags and lithium silicates, as determined by N₂

adsorption-desorption, show isotherms which can be characterised as type II according to the IUPAC classification.⁴ This behaviour corresponds to nonporous materials. The BET surface area was similar for all samples around 1.0 m²/g.

TPC and TPDC for lithium silicates are shown in Figure 3, the CO₂ adsorption and desorption capacity and the inversion temperature can be evaluated. In the case of S-1 Li silicate, a maximum TPC peak is obtained at 516°C while the desorption of CO₂ starts only after 595°C. On the other hand, the desorption peak displays the maximum TPDC at 615°C. In the carbonation process, one can observe a double peak, this double peak is assigned to the formation of outer shell structures consisting in Li₂CO₃ and Li₂SiO₃.⁵ For S-2 Li silicate, a similar inversion temperature was observed with the maximum TPC and TPDC peaks at 557 and 694°C, respectively.

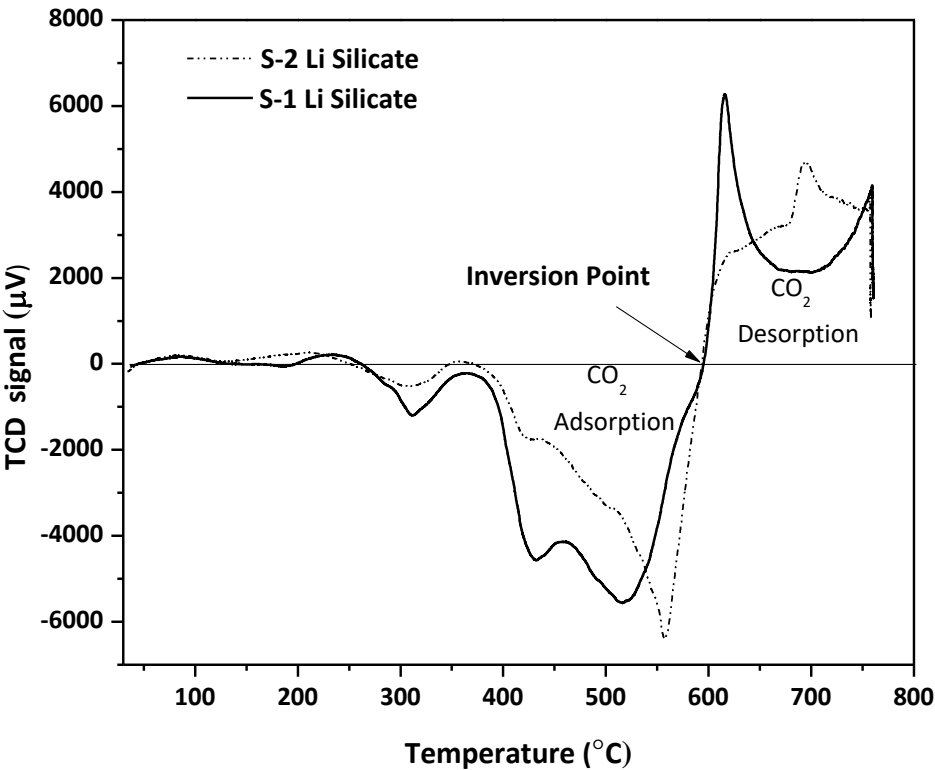


Figure 2: CO₂ adsorption-desorption cycle with respect to temperature (TPC-TPDC)

CO₂-TPD curves at temperatures between 500 and 650°C are shown in Figure 3. The results indicate that the CO₂ adsorption increases with the increase of the temperature until 600°C. The maximum CO₂ capture on the S-1 and S-2 slags-derived lithium silicates was 2.8 and 1.5 mmol of CO₂ per gram at 600°C respectively. At 650°C the adsorption capacity decreases due to the desorption process observed in TPC –TPDC experiments. These differences in the CO₂ capture capacities between both silicates are due to the Li₄SiO₄, which is only identify in S-1 derived lithium silicate.

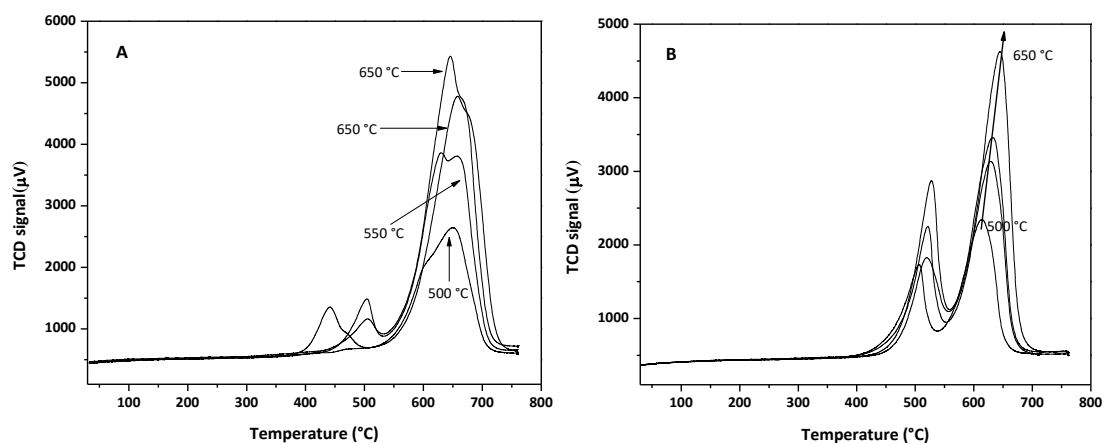


Figure 3: CO₂-TPD profiles of slag-derived lithium silicates with S- 1 (A) y S-2 (B) at temperatures between 500 and 650°C

Conclusions

The preparation of novel lithium based sorbents, prepared using iron and steel slags for CO₂ capture, was achieved in this work. After solid state synthesis, only Li₄SiO₄ was identify in S-1 derived lithium silicate, other lithium compounds were observed in S-2 derived products. TPC-TPDC curves display promising results in terms of CO₂ adsorption and desorption at lower temperatures than other sorbents such as calcite. The inversion temperature of both lithium silicates was lower (595°C) than other lithium and calcium materials.

Acknowledgments

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