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Short communication

Reactions of solid $CaSO_4$ and Na_2CO_3 and formation of sodium carbonate sulfate double salts

Jinsheng Wang*, Yinghai Wu, Edward J. Anthony

CANMET Energy Technology Centre, Natural Resources Canada, 1 Haanel Dr., Ottawa, Ontario K1A 1M1, Canada

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Abstract

High-temperature chemical reactions in mixtures of solid $CaSO_4$ and Na_2CO_3 were investigated in order to explore the mechanisms of enhanced sulfur capture by limestones doped with Na_2CO_3 in fluidized bed combustion. Drastic weight loss of the mixtures was observed in a thermogravimetric analyzer near the melting temperature of Na_2CO_3, indicating chemical reaction. X-ray diffraction analysis for a mixture of the solids following a heat treatment at 850 °C revealed the existence of two sodium carbonate sulfate double salts that have not been reported before for the present system. The formation of Na_2SO_4 in the melt of Na_2CO_3 appears to precede the formation of the double salts. The two double salts are believed to have high porosity and specific surface area similar to those of a better-known double salt, burkeite. The implications of these findings for the enhancement of limestone sulfation by Na_2CO_3 are also discussed.

Keywords: Reaction of solids; Double salts; Limestone; Sulfation; Combustion

1. Introduction

Fluidized bed combustion is a clean combustion technology for coal and other solid fuels. In fluidized bed combustors limestones are used as sorbent to capture SO_2 *in situ*, *via* the following reactions:

$$CaCO_3 = CaO + CO_2 \tag{1}$$

$$CaO + SO_2 + ½O_2 = CaSO_4 \tag{2}$$

This process eliminates the need for costly flue gas desulfurization downstream of the boiler. Unfortunately, utilization of the limestones is low, typically below 40% of their CaO content [1]. The low utilization is believed to be due to a sulfate shell formed on the sorbent particles. The shell is more compact than the porous CaO because of the larger molar volume of calcium sulfate [$46\ cm^3/(mol\ CaSO_4)$ versus $17\ cm^3/(mol\ CaO)$] and retards mass transfer of reactants [1].

It is known that doping the limestone particles with certain inorganic salts (usually by mixing the particles with an aqueous solution of a salt and then drying) can increase the utilization and the sulfation rate. Among such salts, Na_2CO_3 showed the maximum enhancement effect [2,3]. Several mechanisms have been proposed to account for the improvement using such salts. Shearer et al. reported that limestones treated with NaCl showed improved activity in sulfur capture [4]. They proposed that NaCl caused structural changes – pore enlargement in particular – in the solids by forming a liquid phase that increased ionic mobility and diffusion. Stouffer and Yoon attributed the improved sulfation of CaO with Na_2CO_3 additive to formation of CaO with larger pores [3]. Wang et al. suggested salts like Na_2CO_3 could cause lattice defects in the CaO crystal, resulting in enhanced diffusion flux of reactive ions [5]. Laursen et al. considered the effect of Na_2CO_3 to be associated with the formation of a eutectic melt which enhanced ionic diffusion and accelerated molecular rearrangement of CaO [6], and in a later study suggested that increased ionic mobility in the crystal lattice of CaO, due to formation of vacancies when Ca is partly replaced by Na, facilitated structural changes of CaO [7]. A more comprehensive and detailed review has been given recently [8].

The above mechanisms all focus on physical changes in CaO due to the treatment. While the physical changes are quite plausible, we believe the effect of chemical changes should also be considered. Na_2CO_3 has a nominal melting temperature of

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* Corresponding author. Tel.: +1 613 943 7772; fax: +1 613 992 9335.
E-mail address: jiwang@nrcan.gc.ca (J. Wang).

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851 °C, which is in the operating temperature range for the sulfation process in fluidized bed combustion. The melt of Na_2CO_3 is known to react like a strong base [9]. The sulfation product, $CaSO_4$, while having a much higher melting temperature (1450 °C), may dissolve in and react with such a melt. In consequence, reactions such as the following look quite plausible:

$$CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3 \tag{3}$$

$$CaCO_3 = CaO + CO_2 \tag{1}$$

The dissolution and reactions would inhibit the build-up of a sulfate product shell, which normally serves as a barrier to the mass transfer of reactants. The melt would also provide a short circuit for the transfer of ions, which are considered to be crucial in both the sulfation process and the production of morphological changes of the solids [4,10]. In addition, the liberation of CO_2 from the $CaCO_3$ formed by Reaction (3) would create new pores on the surface and enhance mass transfer.

Although Reaction (3) has only been reported for aqueous solutions, using thermochemical software packages (HSC Chemistry and FactSage, for example) a change in Gibbs free energy, ΔG (850 °C) = −33.8 kJ/mol, is obtained, suggesting the plausibility of the reaction between the solids at fluidized bed combustion temperatures.

In this work, reactions between $CaSO_4$ and Na_2CO_3 in the temperature range of fluidized bed combustion have been investigated by thermogravimetric analysis (TGA). As the reaction between $CaSO_4$ and Na_2CO_3 in the temperature range of fluidized bed combustion is expected to result in the release of CO_2 (Reaction (1)), the associated weight loss in a mixture of $CaSO_4$ and Na_2CO_3 powders would be easily detected by TGA. Quantitative X-ray diffractometry (XRD) has been used to identify reaction products. Two sodium carbonate sulfate double salts and CaO have been observed in a $CaSO_4$ and Na_2CO_3 mixture heated to 850 °C, the typical operating temperature of fluidized bed combustion, supporting the occurrence of Reaction (3). The double salts have not been previously reported before for this system, and the effects of their formation on the sulfation performance of the limestones are discussed below.

2. Experimental

TGA was used to detect weight changes in a sample of solid mixtures of $CaSO_4$ and Na_2CO_3 heated in nitrogen gas. The TGA comprised an electronic balance (Cahn 1100), vertical furnace, reactor tube, carrier gas system, and computerized data acquisition system. More details are given elsewhere [11]. The temperature was increased at a rate of 7 °C/min up to 900 °C, encompassing the temperature range of fluidized bed combustion. Reagent grade $CaSO_4$ and Na_2CO_3 were used in the experiments. Reaction products were analyzed by XRD with a Siemens automated diffractometer using Cu Kα_1 radiation (k = 1.5405981 Å). The procedure will be described together with the results.

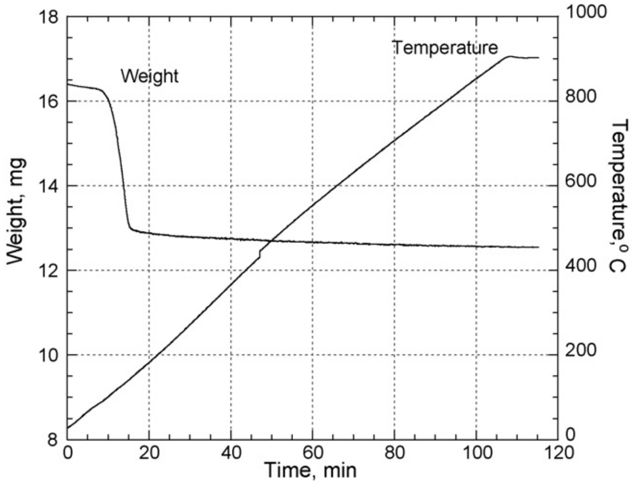

Fig. 1. TGA graph for a sample of $CaSO_4$ dihydrate.

3. Results and discussion

For the TGA study Na_2CO_3 powder was mixed with the powder of the dihydrate form of calcium sulfate $CaSO_4 \cdot 2H_2O$, which would release the water at known transition temperatures and hence give indication of the response and reliability of the system. The TGA results are shown in Figs. 1–3. When the dihydrate alone was heated to 900 °C there was substantial weight loss below 200 °C (Fig. 1), as expected from the nominal temperatures for the transition from dihydrate to hemihydrate (128 °C) and from hemihydrate to anhydrous (163 °C). From 200 to 900 °C only insignificant weight loss occurred, which confirms the stability of the resulting anhydrite under the present conditions. However, when pure Na_2CO_3 was heated there was slow weight loss below 900 °C (Fig. 2), while only above 900 °C did the rate of weight loss increase significantly.

By contrast, for a mixture of Na_2CO_3 and $CaSO_4$, there was a drastic weight loss around 850 °C, suggesting the occurrence of chemical reactions (Fig. 3). About 90% of the weight loss occurred before the temperature reached 900 °C, which

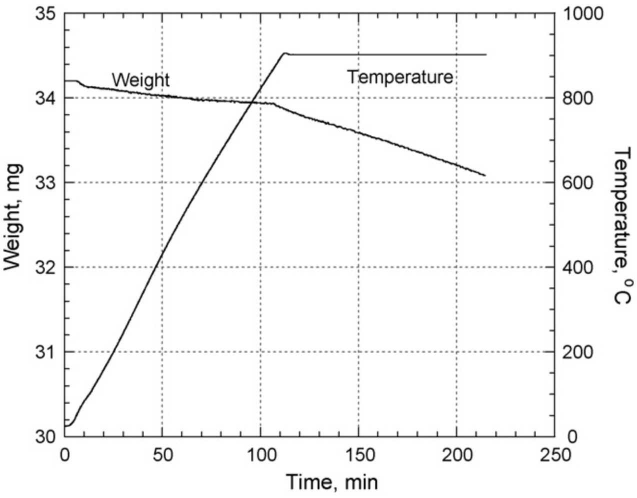

Fig. 2. TGA graph for a sample of Na_2CO_3.

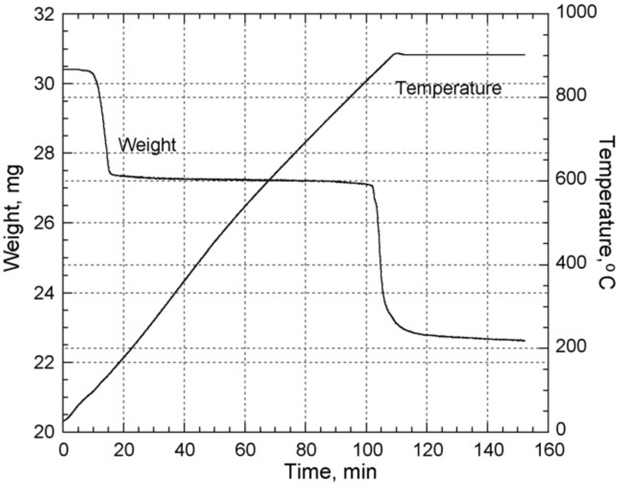

Fig. 3. TGA graph for a mixture of Na_2CO_3 and $CaSO_4$ dihydrate.

Table 1
Results of XRD analyses for a mixture of $CaSO_4$ and Na_2SO_4 heated at 850 °C

Species	wt%
$CaSO_4$	31.9
Na_2CO_3	36.5
CaO	5.9
$Na_6(CO_3)_2SO_4$	14.5
$Na_4CO_3SO_4$	6.4
Crystallinity (wt%)	95.2
Amorphous content (wt%)	4.8

clearly did not occur in the case of pure $CaSO_4$ or Na_2CO_3 (Figs. 1 and 2). As the TGA sample was too small for XRD analysis, a larger sample was prepared by putting a mixture into an oven and heating to 850 °C in air for 40 min. The XRD diffractogram for this sample is shown in Fig. 4, which revealed not only CaO, but also two double salts: $Na_6(CO_3)_2SO_4$ and $Na_4CO_3SO_4$, by comparison of the diffraction pattern to the database of the International Centre for Diffraction Data (ICDD). Weight fractions of the species in the sample determined by the reference intensity ratio (RIR) method are shown in Table 1. The two double salts have not previously been reported in the fluidized bed combustion literature, and there is little information on these salts, but a considerable amount of information on a relatively known double salt, burkeite ($Na_6CO_3(SO_4)_2$), which occurs naturally and can be produced through crystallization from aqueous solutions of Na_2CO_3 and Na_2SO_4.

The appearance of CaO and the two double salts supports the idea that Reaction (3) occurs between $CaSO_4$ and Na_2CO_3. $CaSO_4$ itself has a relatively high melting temperature (1450 °C), and is not likely to participate in reactions that produce the double salts directly. Formation of CaO from decomposition of $CaSO_4$ is implausible below 1050 °C [3]. Therefore, the following is the most likely path to the formation of the double salts and CaO:

$$CaSO_4 + Na_2CO_3(\text{melt}) = Na_2SO_4 + CaCO_3 \quad (3')$$

$$CaCO_3 = CaO + CO_2 \quad (1)$$

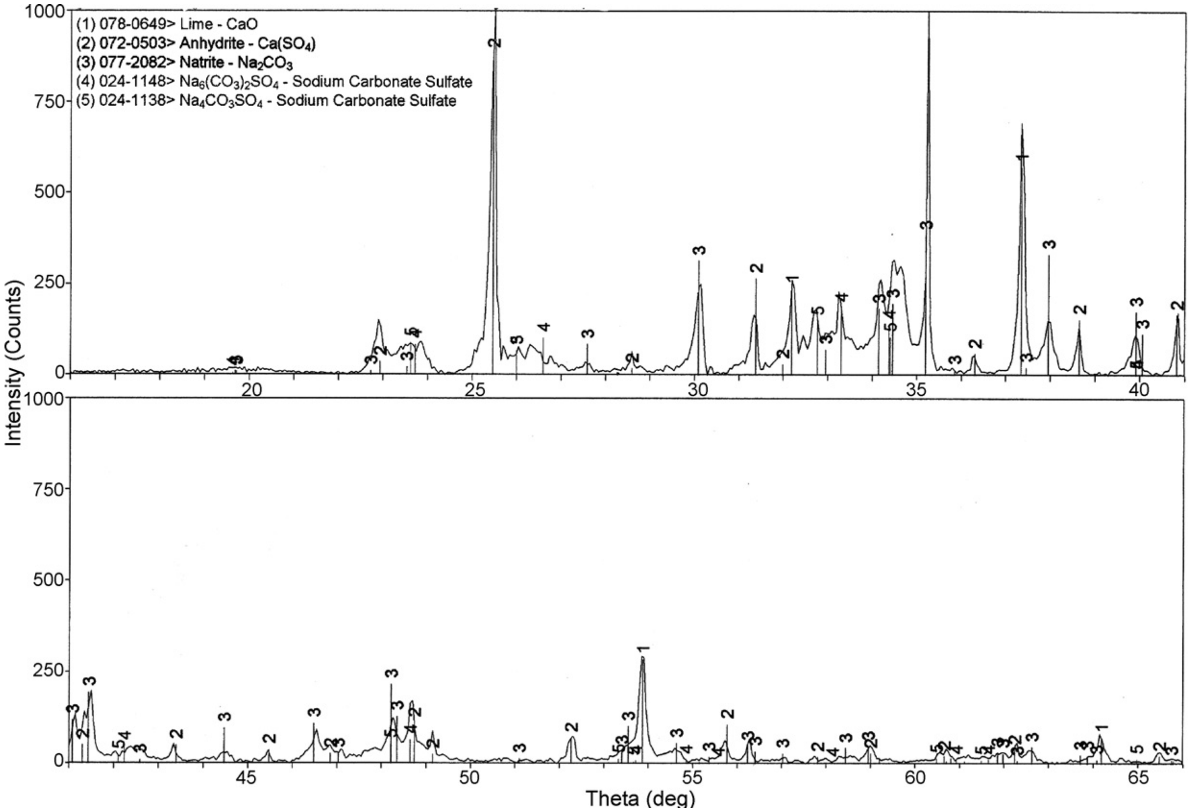

Fig. 4. X-ray diffractogram for a mixture of $CaSO_4$ and Na_2CO_3 after heat treatment at 850 °C.

$$Na_2CO_3 + Na_2SO_4 = Na_4CO_3SO_4 \quad (4)$$

$$2Na_2CO_3 + Na_2SO_4 = Na_6(CO_3)_2SO_4 \quad (5)$$

It should be noted that Na_2SO_4 melts at 884 °C, which is higher than the temperature of the heat treatment employed here for the sample (850 °C). This also suggests that the Na_2SO_4 in Reactions (4) and (5) was formed in the melt of Na_2CO_3.

Little information about the two double salts is available from the literature, but it is known that carbonate- and sulfate-based compounds can be crystallized to form highly porous powders [12]. The aforementioned burkeite is a representative species. Formation of such compounds on the sorbent particles would result in a porous structure with large specific surface area, which is favorable to the sulfation process. As there is nothing known about the high-temperature properties of the two double salts, we do not know whether their solidifications occur in the temperature range of fluidized bed combustion. However, even if the double salts form at lower temperatures, the formation of Na_2SO_4 itself could promote the dissolution of sulfate into the Na_2CO_3 melt, as expected from a comparison of the melting points of Na_2SO_4 and $CaSO_4$ (884 °C versus 1450 °C, respectively), and the knowledge that lower-melting-point species are more soluble when other factors are held constant.

As has been discussed earlier, the solution of sulfate and the local melt environment would inhibit the build-up of the solid product barrier to the mass transfer and facilitate the structural changes of the sorbent particles. Based on this reasoning, adding Na_2CO_3 after the sulfate shell forms on the sorbent particles is not expected to be effective, as in this case the dissolution of $CaSO_4$ would only occur on the surface and any effect on the shell would be limited. This view is consistent with the observation that treating presulfated limestone particles with Na_2CO_3 and then resulfating the particles resulted in only small increases in the degree of sulfation [6].

The process discussed above is not likely to be the sole mechanism for the enhancement of sulfur capture. Instead we suggest that several mechanisms contribute to enhancement in the sulfation process. Nevertheless, melts that result in chemical transformations are likely to show a greater effect on the activity of the sorbent. This might explain the observation that Na_2CO_3 is the most effective additive for enhancing sulfation in this system.

4. Conclusions

Experimental results show that $CaSO_4$, which forms during sulfation of limestone sorbent, can react with Na_2CO_3 over the temperature range typical of fluidized bed combustion. While more work is required for a conclusive elucidation of the effects of the reactions on enhancement of sulfur capture, observations made in the present study indicate the occurrence of reactions in the solid mixture of Na_2CO_3 and $CaSO_4$ near 850 °C; and formation of $Na_6(CO_3)_2SO_4$, $Na_4CO_3SO_4$ and CaO. The two double salts appear to be produced in such mixtures, at a temperature lower than the melting point either of $CaSO_4$, or of Na_2SO_4.

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