

SULFUR REDUCTION FROM CARBONATE-SULFATE MELT

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Sulfur emission in the form of SO₂ in flue gas is the most serious pollutant associated with coal combustion. Calcium carbonate sulfur scrubbing, the process most commonly in use today, is costly, produces large amount of waste and leaves a considerable amount of SO₂ in the gas. The carbonate eutectic method for removing SO₂ from flue gas at 450–650 °C was initially proposed in the 1970's, but despite its great efficiency could not be used due to the complexity of the carbonate melt regeneration stage. We propose a simple ways to remove sulfur from the carbonate eutectic melt by purging it with CO (chemical process) or sulfate electrolytic reduction to elemental sulfur (electrochemical process).

Chemical process by purging with CO.

This process reaction leads to the reduction of sulfate to carbonyl sulfide gas that leaves the melt, rather than to sulfide ions that remain in the melt. The experiments conducted show that nearly complete sulfur removal from the melt is possible at 550 °C and that the reaction rate is sufficiently high for a large scale process. The proposed modifications provide solutions to two critical issues: (i) at 550 °C there is no problem of corrosion because a reaction cell of stainless steel with high chromium content is stable with respect to the carbonate eutectic melt at that temperature and (ii) removal of sulfur in the form of COS, rather than H₂S, provides considerable freedom in choosing the final product: either sulfuric acid or elemental sulfur.

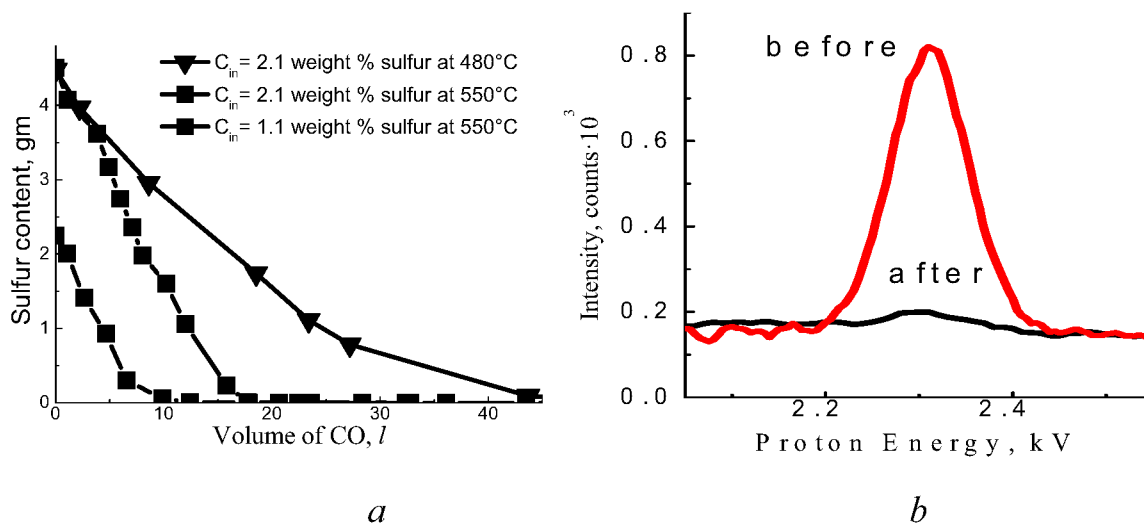


Figure 1. *a* – Removal of sulfur from the Li-Na-K carbonate melt, initially containing 1.1 and 2.1 weight% of sulfur, by flowing CO at 550 °C and 480 °C; *b* – Region of EDS spectra between 2.2 and 2.4 eV, showing the S-related peak for a melt with initial sulfur content 1.1 weight % before and after treatment with CO at 550 °C

A ternary Li₂CO₃-Na₂CO₃-K₂CO₃ eutectic mixture was mixed with 4.8 to 9.1 % Na₂SO₄ and melted at 550 °C. This concentration range of sulfate was chosen

based on the data on SO₂ absorption by the carbonate eutectic to simulate the melt after SO₂ scrubbing. The preparation of the eutectic and the subsequent measurements were carried out in a welded, hermetic titanium cell. After purging the system with pure nitrogen, CO gas was introduced into the free volume above the melt. Samples of the electrolyte were taken with a cold rod and then analyzed with energy dispersive X-ray fluorescence spectroscopy. The exhaust from the reaction cell was captured in a liquid trap containing KOH and H₂O₂. COS may be identified by precipitation of elemental sulfur according to the reaction with KOH and H₂O₂. Any obtained precipitate was filtered and recrystallized at 130°C in order to enable EDS analysis in the SEM.

Electrochemical process.

In the electrochemical regeneration process elemental sulfur was produced in the cathode space of the electrolyzer at 800 °C. As a composite material for the reactor, pipes and electrodes, we chose titanium. On the Figure 2 shown temperature effect on the Gibbs energy and decomposition potential for reactions:

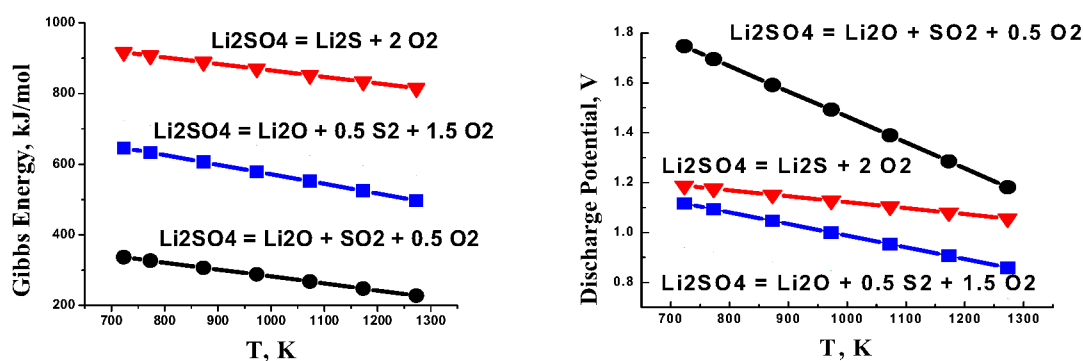
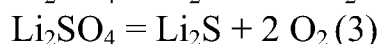
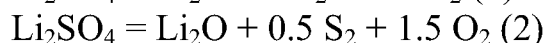
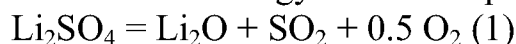


Figure 2. Results of the thermodynamic calculations

One has to note that the Gibbs energy for all reactions is of great positive value and Gibbs energy of reaction (1) is much smaller in absolute value than the Gibbs energy of reactions (2,3), but given the fact that the reaction (2) requires exchange of six electrons (from S⁺⁶ to S⁰), the reaction (3) requires exchange of eight electrons (from S⁺⁶ to S⁻²), and the reaction (1) only two electrons (from S⁺⁶ to S⁺⁴), the decomposition potential of lithium sulfate decomposition to elemental sulfur is significantly lower than decomposition potential of lithium sulfate decomposition to SO₂ and to Li₂S.

Current-voltage (I–V) experiments were conducted with Ti working electrodes at 800 °C.

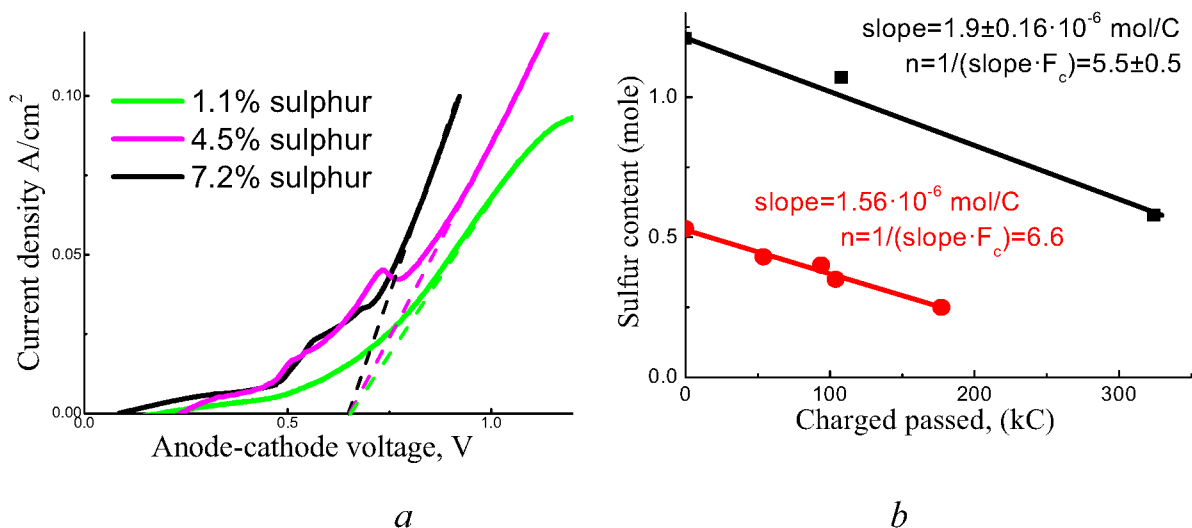


Figure 3. *a* – Experimentally determined decomposition potential of sulfate in the Li-Na-K carbonate eutectic at 800 °C. Note: The decomposition potential does not depend on the sulfur content. Dashed lines are approximations of the decomposition potential for sulfur content from 1.1 % to 7.2 %; *b* – Decrease of the sulfur content in the carbonate melt under current

For prolonged electrolysis we used the titanium electrolytic cell; gas space of the anode compartment was separated from gas space of the cathode compartment, but carbonate-sulfate salt melt was a common. The initial amount of melt was 500 gr. Both electrodes were made of titanium. Before the beginning of the electrolysis, both cathode and anode compartments were purged by nitrogen.

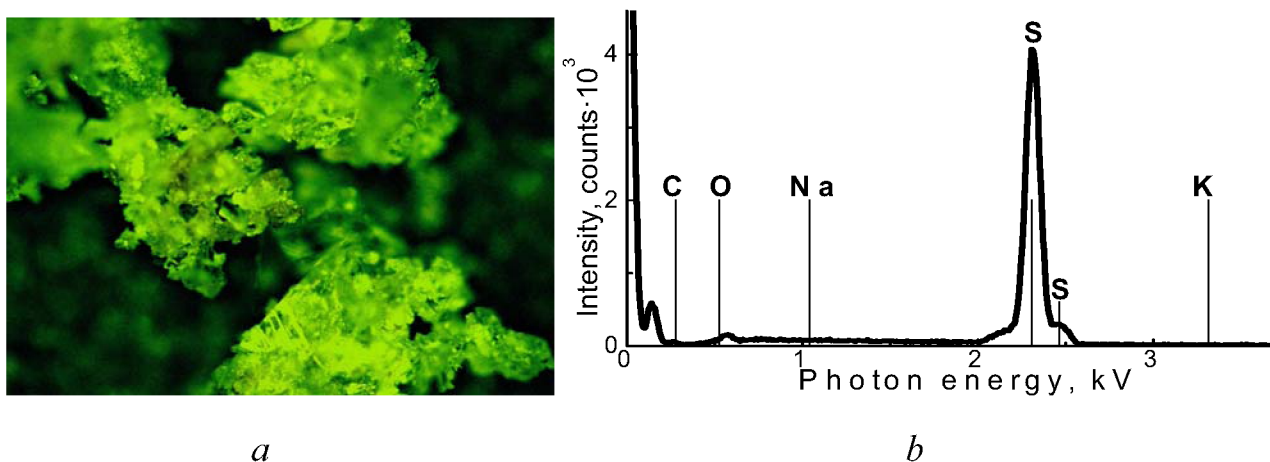


Figure 4. *a* – optical image of the obtained sulfur crystals and (*b*) their EDS spectrum. The width of the image in (*a*) corresponds to 1 mm. To obtain large crystals for EDS analysis, the filtered sulfur precipitate was recrystallized above 130 °C

One can foresee that the carbonate melt-based SO_2 removal technique may become a practical and viable method for limiting sulfur emission to the atmosphere.