

**ANNUAL PROJECT REPORT  
AS OF DECEMBER 1992**

**1. PROJECT SPONSOR:**

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**2. PROJECT MANAGER:**

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**3. OCDO GRANT NO#:** R-902-4

**4. PROJECT:** Final Report

**5. PROJECT TITLE:** "PRODUCTION OF ELEMENTAL SULFUR FROM SPENT SORBENT AND CO<sub>2</sub>"

**6. PROJECT TERM:** FROM April 1, 1992 TO March 31, 1994

<b>7. PROJECT</b>	<b><u>NAME</u></b>	<b><u>COST-SHARE</u></b>
<b>CO-SPONSORS:</b>	OCDO	\$64,940
	University of Cincinnati	<u>30,896</u>
<b>TOTAL PROJECT COST:</b>		\$95,836

**I. ABSTRACT**

**8. OBJECTIVES**

The objective of this project is to study the feasibility of producing elemental sulfur from a spent solid sorbent and carbon dioxide (CO<sub>2</sub>) gas. The spent solid sorbent derives from a novel coal desulfurization process currently under development by OCDO and the U.S. DOE and consists mainly of calcium sulfide (CaS) with trace quantities of unreacted lime (CaO) and limestone (CaCO<sub>3</sub>). In the proposed method, CaS is first dissolved in a solution of acetic acid (CH<sub>3</sub>COOH) forming a solution containing primarily hydrogen sulfide (H<sub>2</sub>S), calcium ions (Ca<sup>+</sup>), and acetic ions (CH<sub>3</sub>COO<sup>-</sup>). The H<sub>2</sub>S is subsequently stripped from the solution using carbon dioxide (CO<sub>2</sub>) (available from the stack gas) and the gaseous H<sub>2</sub>S-CO<sub>2</sub> mixture is then catalytically converted to elemental sulfur, methane (CH<sub>4</sub>), and water vapor. The sorbent can then be recovered from the remaining solution after stripping off the H<sub>2</sub>S that was dissolved in solution.

The advantages of this scheme are 1) Production of low cost elemental sulfur rather than sulfuric acid which is preferable from storage and resource recovery standpoint, 2) Regeneration of the calcium based sorbent for reuse in the coal desulfurization unit, 3) Production of a usable fuel (methane), and 4) Consumption of CO<sub>2</sub>, a green house gas which has been found to affect global warming.

## **9. WORK DONE AND CONCLUSIONS:**

Solubility experiments have been performed to determine the solubility of calcium sulfide (CaS) in different concentrations of formic (HCOOH) and acetic (CH<sub>3</sub>COOH) acid. It was found that CaS had a higher solubility in acetic acid; therefore this acid is being studied for use in the stripping step. Also, the solubility of CaS increases and the Ph of the solution decreases with increasing acid concentration.

The experimental apparatus for the stripping experiments has been designed and built and experiments have been completed which have shown that over 90% of the H<sub>2</sub>S can be recovered.

The feasibility of using a cobalt-molybdenum (Co-Mo) sulphide catalyst that was prepared from a commercial Co-Mo oxide catalyst for the production of elemental sulfur from hydrogen sulphide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>) in a packed bed catalytic reactor was studied in the laboratory. It was demonstrated that the desired sulphide catalyst could be prepared by first reducing, then sulphiding the corresponding oxide. The results showed that the prepared catalyst was capable of producing elemental sulfur from the thermal decomposition of H<sub>2</sub>S in the presence of CO<sub>2</sub> over a temperature range of 465-575°C (870-1070°F) and at atmospheric pressure. Since equilibrium was not reached inside the reactor, the specific rate coefficient was calculated as well as the Arrhenius parameters. In addition, the H<sub>2</sub>S decomposition reaction was found to be a second order reaction and have an activation energy of 120 kJ/mol (28.6 kcal/mol).

## **10. PLANS FOR COMING YEAR:**

This project has been completed.

## **II. HIGHLIGHTS/ACCOMPLISHMENTS**

11. It was found that H<sub>2</sub>S could be prepared and recovered from CaS waste solids.

A review of the different catalysts that would be suitable for conversion of H<sub>2</sub>S and CO<sub>2</sub> to elemental sulfur has been done. Tests have shown elemental sulfur can be obtained at temperatures as low as 500°C.

## **III. ARTICLES/PRESENTATIONS**

12. Production of Elemental Sulfur form the Thermal Decomposition of H<sub>2</sub>S in the Presence of CO<sub>2</sub>, D. Soriano, T. Keener and S. Khang. Submitted to *Chemical Engineering Communications*.