

ADVANCED BYPRODUCT RECOVERY:

DIRECT CATALYTIC REDUCTION OF SULFUR DIOXIDE TO ELEMENTAL SULFUR

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Introduction

More than 170 wet scrubber systems applied to 72,000 MW of U.S., coal-fired, utility boilers are in operation or under construction. A small fraction (of order 1 percent) of these systems produce a useable byproduct (gypsum); the remainder generate approximately 20 million tons per annum of disposable flue gas desulfurization (FGD) byproduct, which are transported and disposed of in landfills. The use of regenerable sorbent technologies has the potential to reduce or eliminate this solid waste production, transportation and disposal.

All regenerable FGD systems produce an off-gas stream from the regenerator that must be processed further in order to obtain a saleable byproduct, such as elemental sulfur, sulfuric acid or liquid SO₂. This off-gas has only a fraction of the flue gas volume, and contains no oxygen. Recovery of sulfur from this stream in a single-stage catalytic converter, avoiding a multi-stage Claus plant, could decrease the cost and accelerate the commercialization of many regenerable FGD processes.

The team of Arthur D. Little, Tufts University and Engelhard Corporation are conducting Phase a four and a half year, two-phase effort to develop and scale-up an advanced byproduct recovery technology that is based on a direct, single-stage, catalytic process for converting sulfur dioxide to elemental sulfur. This catalytic process reduces SO₂ over a fluorite-type oxide such as ceria and zirconia.

Background

In previous DOE-supported work, the activity and selectivity of fluorite-type oxides, such as ceria and zirconia, for reduction of SO₂ were investigated. A wide range of transition metal-impregnated ceria and zirconia catalyst formulations were evaluated in a packed bed reactor, under both dry gas and wet gas (2% H₂O) conditions. Under dry gas conditions, more than 95% yield of elemental sulfur and essentially complete SO₂ conversion were obtained for a variety of catalysts. Under wet gas conditions, Cu/CeO catalyst showed the lowest light-off temperature, the greatest resistance to water, and gave over 90% SO conversion and more than 70% elemental sulfur yield.

Based on these results, and the fact that a 25 hour test indicated that the Cu/CeO catalyst was stable at the reacting conditions, the Cu-Ce-O system was selected for detailed studies of the SO₂ reaction with CO. The effects of copper content, temperature, presence of water, and presence of CO₂ on the selectivity and activity of this catalyst system were evaluated. This work led to the selection of bulk (Ce_{0.85}(La)_{0.15})O_x for further study. More than 95% elemental sulfur yield, corresponding to almost complete sulfur dioxide conversion, was obtained over a Cu-Ce-O oxide catalyst with a feed gas of stoichiometric composition ([CO] / [SO₂] = 2) at temperatures above 450°C. This catalyst showed no apparent deactivation during a

35-hour run in the presence of 2% water at 470°C. In addition, the performance of this catalyst with other reducing gases was briefly investigated. Elemental sulfur yields of 50 - 66% were obtained using CH₄ at 600°C and an elemental sulfur yield of 72% was obtained using C₂H₆ at 800°C. It is noteworthy that all tests mentioned above were conducted at high space velocities, on the order of 40-50,000 (SHP).

Thus previous work has shown that the catalytic activity of fluorite-type oxides, such as ceria and zirconia, for the reduction of sulfur dioxide by carbon monoxide to elemental sulfur can be significantly promoted by active transition metals, such as copper. This type of mixed metal oxide catalyst has stable activity and is resistant to water and carbon dioxide poisoning. The performance of the catalyst was consistently good over a range of SO₂ inlet concentration (0.1 to 10%) indicating its flexibility in treating SO₂ gases as well as high concentration streams.

Objectives and Approach

The overall objective of the current two-phase program is build on the results described above to advance the SO₂-reduction technology from the laboratory to commercial scale. The principal objective of our Phase I program is to identify and evaluate the performance of a catalyst which is robust and flexible with regard to choice of reducing gas (methane, carbon monoxide, or syn-gas). In order to achieve this goal, we have planned a structured program which includes a market/process/cost evaluation, lab-scale catalyst preparation/optimization experiments, bulk or supported catalyst kinetic studies and bench-scale catalyst/process experiments. The work as a whole will be directed towards rapid scale-up and commercialization of the system, with guidance being provided by the results of our market, process and cost evaluation and by Engelhard Corp.

Regenerable FGD Process Evaluation

The purpose of this effort is to provide key performance and commercial input at the beginning of the catalyst development effort. Interviews are being conducted with regenerable sorbent system developers and with electric utilities to define key market issues, such as: preferred reducing gas; variability of off-gas stream composition; system contaminants; emissions limitations; cost constraints; and reliability/durability issues. From the interview responses, key performance criteria for the system will be defined. The performance and cost of the proposed catalytic process will be evaluated and compared to these criteria. In addition, these performance criteria will be used to define milestones and to focus catalyst and process development.

To date, a survey has been conducted to develop a compendium of FGD technologies capable of producing enriched streams of recovered SO₂ and of processes capable of converting the recovered SO₂ to elemental sulfur. The survey focused on identifying those processes that have achieved commercial application; have attained an advanced stage of development (typically successful prototype testing), whether still actively being pursued or not; or, are currently under active development at a level beyond laboratory scale. The purpose of the survey was twofold. First, to establish the database for the range of potential feedstream conditions and most probable, or preferred, reducing gases. And, second, to begin to develop the background information for assessing the market potential for one-step SO₂-sulfur conversion technology.

Preliminary Survey Results

There are about two dozen advanced FGD technologies producing an enriched SO₂ product stream. In general, they fall into four major groups, although most of these have subgroups that further differentiate general process approaches: (1) Aqueous alkaline scrubbing (alkaline metal-based and ammonia-based);

(2) Organic absorption (amine-based processes and citrate-based processes); (3) Reactive adsorption (zinc-based, copper oxide-based and alkali-metal-based) and (4) Physical adsorption (activated carbon).

With the possible exception of the alkali metal-based reactive adsorption processes, notably Sorbtech and NOXSO, almost all of the technologies could benefit from an efficient, cost-effective, one-step sulfur conversion technology. The conditions of the byproduct SO₂ streams vary widely- from highly concentrated streams (95% SO₂) at low temperature with residual moisture, to low concentration streams (1-2% SO₂), some at high temperature with various levels of "contaminants".

In order to focus research and development efforts, we are in the process of prioritizing the FGD technology groupings to establish a profile of feedstream characteristics most representative of commercialization needs. Consideration is being given to a variety of factors including: the FGD technology development status; the benefits/importance of an add-on sulfur conversion technology to the commercialization of the technology; the current level of support in advancing the technology; and, in concert with the assessment of the critical market forces, the perceived opportunities for the FGD technology were it to be successfully demonstrated. The initial prioritization places technologies into two general categories.

Primary: Technologies in this category are ones at advanced stages of development and which continue to be actively pursued, or technologies which have been commercialized and continue to be actively marketed; but, only those without close-coupled sulfur conversion processes are considered. They include zinc-based technologies--currently pursued as the technology of choice for Integrated Gasification Combined Cycle applications; the copper oxide process--one of the most advanced regenerable technologies for byproduct SO₂ that continues active development; and carbon-based adsorption--a well-advanced technology that has been through demonstration programs.

Secondary: These are technologies that have achieved a significant level of commercialization (defined as a number of installations which are still operated) but are not now actively marketed; or have progressed through pilot testing and offer significant potential advantages, but whose development is currently stalled. They include: selected aqueous alkali processes-- as a group these have not fared especially well for sulfur conversion and currently only the ELSORB and SOXAL processes are being actively pursued; ammonia scrubbing--most of the applications for ammonia scrubbing are for fertilizer byproducts, however the potential remains for conversion to sulfur; and selected amine-based processes--two of the (the Dow technology and CANSOLV) may offer significant advantages over prior processes.

Catalyst Preparation and Optimization Studies

Work to date has focused on screening tests of a variety of catalyst formulations. The catalyst preparation technique used consists of mixing a solution of nitrate salts and urea and heating the solution to 100°C under strong stirring. Co-precipitation occurs as the solution is heated for 8 hr. The precipitate is then filtered, washed twice with hot deionized water, dried overnight, and then calcined in air at 650°C for 3 hr.

Catalysts with nominal metal content 15 at%, namely 15% Cu-Ce(La)-O, 15% Co-Ce(La)-O, 15% Ni-Ce(La)-O, and Ce(La)O₂, were chosen for initial activity tests using methane reductant. Subsequent elemental analysis identified 15 at% Cu, 6 at% Co, and 2 at% Ni on the corresponding bulk oxide catalysts. The apparatus used in these experiments is the same packed-bed micro-reactor used in the prior work described above. The reactor consists of a 0.6 cm I.D. 50 cm long quartz tube with a porous quartz frit placed at the middle for supporting the catalyst. The reactor tube is heated by a Lindberg furnace and temperature-controlled. The reacting gases and helium are mixed prior to the reactor inlet and the resulting

gas mixture flows downward through the packed bed. Water vapor is introduced by bubbling the helium through a heated water bath. The pressure drop of gas flowing through the assembly is small, thus the experiments are carried out essentially at atmospheric pressure. A cold trap installed at the outlet of the reactor is used to condense out the elemental sulfur from the product gas stream. The product gas, free of sulfur and particulate matter, is analyzed by a gas chromatograph with a Thermal Conductivity Detector (TCD).

Initial activity tests were performed under the following conditions: stoichiometric amount of reacting gases, which consist of 1% SO_2 and 0.5% CH_4 (balance He) at a total flow rate of 100 cm^3/min . The contact time was 0.09 gs/cm^3 which corresponds to a space velocity of approximately 80,000. The fresh catalysts are typically activated by heating for one hour in 9.9% CO/He at 600°C. After activation the reacting gases were introduced at 600°C and the reaction temperature was raised to about 780°C in steps of 50°C. Both light-off and fall-off behavior were examined to check for possible hysteresis effects and deactivation.

Ni, Co, Cu, Mn, Cr, and Fe containing $\text{Ce}(\text{La})\text{O}_x$ and $\text{Zr}(\text{Y})\text{O}_2$ catalysts, as well as pure CeO_2 and $\text{Ce}(\text{La})\text{O}_2$ were tested using reacting gases at stoichiometric ratio. All tests were performed at a gas flow rate of 100 cm^3/min , at contact times of 0.09 gs/cm^3 and 0.18 gs/cm^3 , and in the temperature range 500°C to 750°C. Results of these screening experiments are shown in Figure 1. The results are shown in terms of sulfur dioxide conversion, $X-\text{SO}_2$ and elemental sulfur yield, $Y-[S]$, defined as follows:

$$X - \text{SO}_2 = \frac{([\text{SO}_2]_0 - [\text{SO}_2])}{[\text{SO}_2]_0} \qquad Y - [S] = \frac{[S]}{[\text{SO}_2]_0}$$

where $[\text{SO}_2]_0$ and $[\text{SO}_2]$ are the inlet and outlet sulfur dioxide concentrations, respectively, while $[S]$ is the outlet elemental sulfur concentration. $[S]$ is calculated from the difference:

$$[S] = [\text{SO}_2]_0 - [\text{H}_2\text{S}] - [\text{COS}] - [\text{SO}]$$

$\text{Ni}-\text{Ce}(\text{La})-\text{O}_x$ catalyst showed the highest activity, even at relatively low Ni concentrations (2%). Figure 2 shows the effects of molar ratio R of CH_4/SO_2 on the activity and selectivity of $\text{Ni}_{0.02}[\text{Ce}(\text{La})]_{0.98}\text{O}_x$. $R=0.5$ indicates a stoichiometric mixture. Although the SO_2 conversion ($X-\text{SO}_2$) increases to essentially unity as an excess of CH_4 is supplied ($R=1$ or 1.5), the sulfur yield levels off at about 50-60%, leading to significant amounts of H_2S and, to a lesser extent, COS in the reactor outlet stream. Figure 3 shows the effects of temperature and contact time (space velocity) on the activity and selectivity of $\text{Ni}_{0.02}[\text{Ce}(\text{La})]_{0.98}\text{O}_x$. At long contact times and above 650°C, the selectivity to elemental sulfur drops (see difference between $X-\text{SO}_2$ and $Y-[S]$). At these conditions H_2S (and to a lesser extent COS) are also formed. However, at all other conditions, selectivity to sulfur exceeds 95%, and is typically 99%.

Conclusions and Future Work

Prior work on direct reduction of SO_2 to elemental sulfur over $\text{Cu}_{0.15}[\text{Ce}(\text{La})]_{0.85}\text{O}_x$ catalyst using CO as a reducing gas has been extended to include tests with methane reducing gas. For reduction using methane, results to date indicate that a Ni promoter is very good at low levels and good performance has been demonstrated using $\text{Ni}_{0.02}[\text{Ce}(\text{La})]_{0.98}\text{O}_x$. The low reactivity of CH_4 compared to CO led to significantly higher light-off temperatures (700-750°C vs. 450-550°C for 90%+ conversion of SO_2) (at 25 at%) was not as good a promoter, apparently due to agglomeration/sintering of CuO particles. Experiments with low levels of Cu in CeO_2 are planned for comparison. Catalysts containing Cu, Co, Ni and Mn will continue to

be examined. The effect of water vapor will be examined on the best of each catalyst type. Tests will also be conducted with other reducing gases, such as synthesis gas. Promising catalysts will be selected for tests in supported form.

A bench-scale reactor test system is also under fabrication at Arthur D. Little. This system will be used to evaluate supported catalyst (honeycomb or pellet). The reactor internal dimensions are 5 cm diameter \times 100 cm long. Continuous on-line measurements of reactor gas composition will be performed. The supported catalysts to be tested at Arthur D. Little will be fabricated by Engelhard based on the formulations developed at Tufts. The bench-scale test system is designed to simulate off-gas streams representative of the range of regenerable processes identified in our survey.

References

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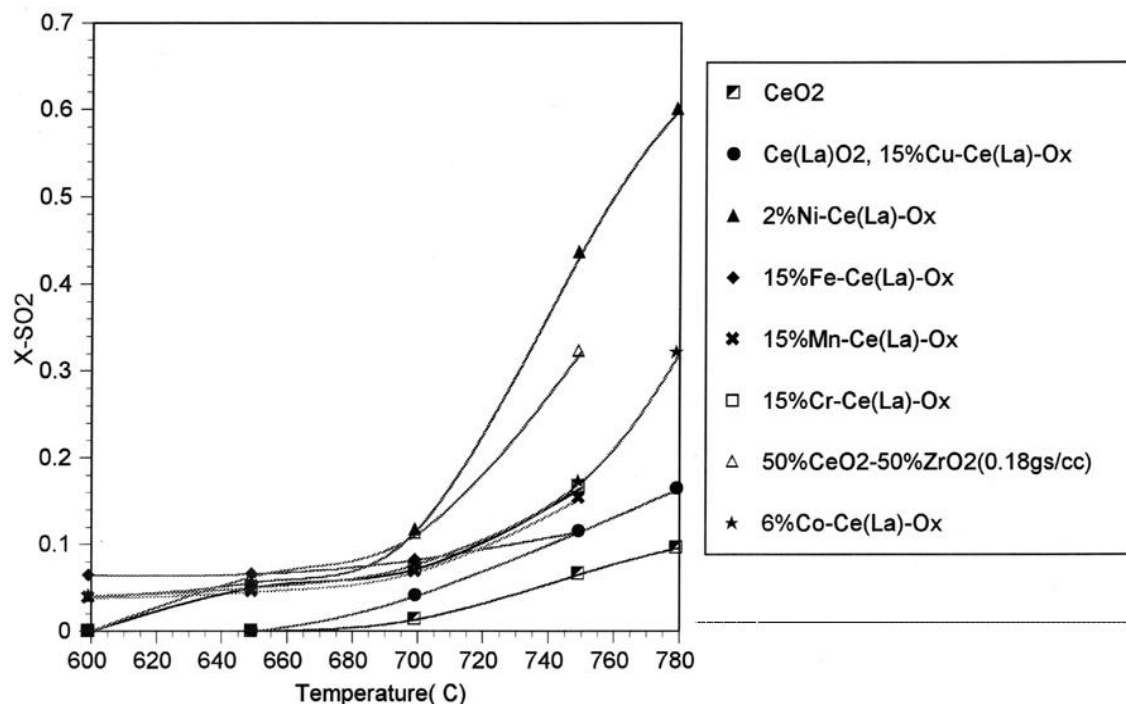


Figure 1. Results of screening experiments in 1% SO₂ / 0.5% CH₄ (balance He), contact time = 0.09 gs/cc (approximately 80,000 h⁻¹), pre-reduced in 9.9% CO/He at 600°C for 1 hr.

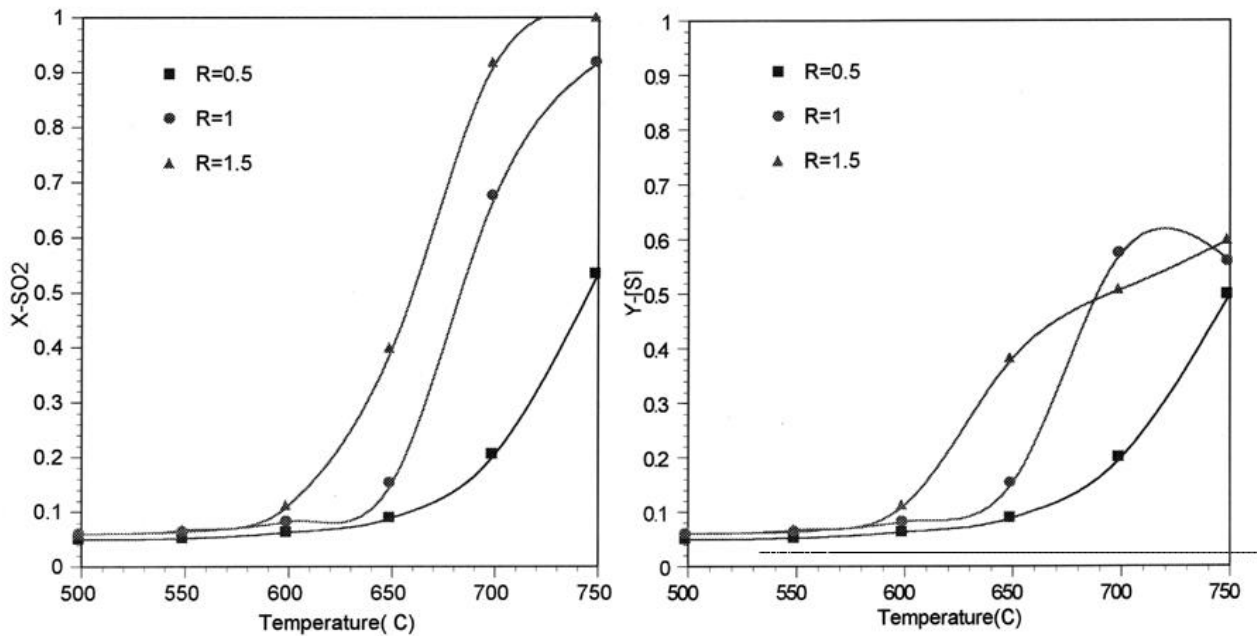


Figure 2. The effect of molar ratio R ($\text{CH}_4 / \text{SO}_2$) on the activity of $\text{Ni}_{0.02}[\text{Ce}(\text{La})]_{0.98}\text{O}_x$. 1% SO_2 , contact time = 0.18 gs/cc (approximately $40,000 \text{ h}^{-1}$), pre-reduced in 9.9% CO/He at 600°C for 1 hr

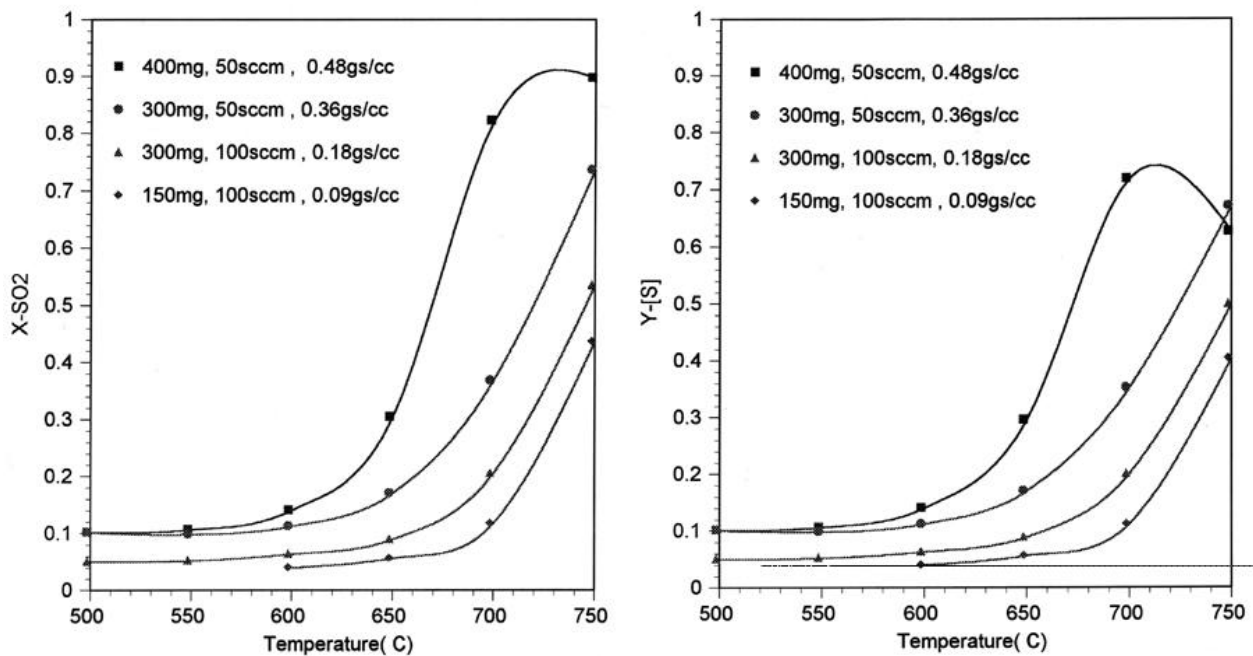


Figure 3. The effect of contact time on the activity of $\text{Ni}_{0.02}[\text{Ce}(\text{La})]_{0.98}\text{O}_x$. 1% $\text{SO}_2 / 0.5\% \text{CH}_4$ (balance He), pre-reduced in 9.9% CO/He at 600°C for 1 hr.