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**Emissions R&D at GE/CRD
Coal-Fueled Diesel: Technology Development
Methods for SO₂ and NO_x Removal From Coal Diesel Exhaust**

Topical Report

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Work Performed Under Contract No.: DE-AC21-88MC23174

**For
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October 1993

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Section 1

SUMMARY

Four processes were investigated at the GE Research and Development Center (GE-CRD) for the removal of gaseous pollutants from the exhaust of a coal-fired diesel locomotive engine. The minimum goal for emissions control was to reduce the pollutant levels at least to the levels of a conventional diesel engine. It should be noted, however, that some of the methods investigated were capable of reducing emissions below these levels. Achieving the minimum goal requires a reduction of approximately 50% in SO_2 emissions and a 90 to 95% reduction in particulate emissions, the actual percentages varying with the fuel. NO_x emissions from the coal diesel are approximately 50% of the conventional diesel level.

The space limitations on board the locomotive present the greatest obstacle to the design of an emissions control system. The cleanup system must be compact as well as multifunctional. The development of a particulate collection device was undertaken by GE Environmental Services, Inc. (GEESI). Among the options they evaluated were high-temperature metal filters, cyclones, and a granular bed. The development of a cleanup method for SO_2 and possibly NO_x was undertaken at GE-CRD. A process was sought which could incorporate one of the particulate removal devices under consideration.

Four processes utilizing three classes of sorbents — copper oxide, calcium-based, and sodium bicarbonate — were investigated for SO_2 capture. Two of these processes use copper oxide (CuO), a regenerable SO_2 sorbent. The CuSO_4 formed has the added property that it catalyzes the reduction of NO_x to N_2 in the presence of NH_3 . This NO_x removal capability was tested for both CuO processes. One process uses a granular bed of CuO pellets, which can also be used as a particulate removal device, either alone or in conjunction with cyclones upstream. The other process involves the injection of CuO powder into the engine exhaust. The reacted sorbent and exhaust particulates would both be captured downstream by high-temperature metal filters. Both

processes would require that regeneration of the sorbent occur off the locomotive. In the other two processes, disposable, powdered sodium bicarbonate and calcium-based sorbents would be injected into the exhaust for SO_2 removal only. As with the CuO , these sorbents would also be captured downstream on high-temperature filters.

Laboratory tests were performed to evaluate all three classes of sorbents for SO_2 removal and the copper oxide sorbent for NO_x removal. Test results indicate that for SO_2 removal alone, sodium bicarbonate is the most efficient sorbent. Greater than 94% SO_2 capture was achieved with 63% utilization of the sorbent; greater than 97% with 49% sorbent utilization.

Greater than 90% SO_2 reduction and greater than 90% NO_x reduction were attained simultaneously with copper oxide, both in the granular bed and with powder injection. Powder injection is the more feasible of the two processes because it can more easily be integrated with a particulate cleanup device. Even for the powder injection, however, the ability to remove NO_x does entail certain penalties. Although copper oxide is regenerable, the regeneration process itself adds logistical complexity to a locomotive-scale cleanup system. There is not enough space on the locomotive to regenerate the copper oxide. Regeneration stations would have to be located along the railroad routes at refueling stops. Another disadvantage of using copper oxide is that up to seven times as much sorbent by weight is required compared with sodium bicarbonate because the copper oxide is present in a 10% concentration on an inert carrier while the sodium bicarbonate is 100% reactive. Nonetheless, if NO_x control is desirable, copper oxide can achieve substantial removal of NO_x and SO_2 simultaneously. It was the only option considered.

Two calcium-based sorbents — an atmospherically slaked, hydrated lime and a pressure-slaked, dolomitic, hydrated lime — were investigated and found not to be very effective for SO_2 removal under expected operating conditions. Because the maximum SO_2 capture achieved was only 40%, these two sorbents were not considered suitable for use in a locomotive emissions control system.

Section 2

INTRODUCTION

In an effort to find new applications for U.S. coal reserves, the U.S. Department of Energy (DOE) has sponsored General Electric Company in the development of a full-scale, coal-fueled diesel locomotive. In this application, conventional diesel fuel is replaced by coal water slurry (CWS), a 50/50 mixture by weight of micronized coal and water. The use of this alternative fuel has required major redesign of the diesel engine as well as a number of other locomotive subsystems. In addition the use of a coal fuel requires an emissions control system on board the locomotive. Because there is no space available for the emissions control system on a conventional locomotive, the coal locomotive was lengthened 10 ft to include space for a cleanup system. This extra space was 7 ft wide, 7 ft high, and 10 ft long, a volume of roughly 500 ft³. Even with this added volume, however, it was extremely difficult to fit a cleanup system on the locomotive.

GE Transportation Systems (GETS) is the prime contractor responsible for overall locomotive systems development and testing. GE Environmental Services, Inc. (GEESI) and GE Corporate Research and Development (GE-CRD) are both subcontractors in this effort. GEESI has responsibility for design of the full-scale locomotive emissions system. GE-CRD is involved in developing technologies for the fuel injection system, wear-resistant materials, and the emissions system.

At present, emissions from diesel locomotives — coal or conventional — are not regulated. There is, therefore, no way to know how clean coal-diesel exhaust will have to be. For the work described here, the decision was made that the coal-diesel exhaust should be cleaned to at least the current level of a conventional diesel. Table 2.1 lists the properties of the coal found in the CWS.

Table 2.1 Otsica Coal Water Slurry Properties

Ash, %	0.76–0.87
Solids, %	49.6–50.4
Volatiles, % dry	38.0–39.0
Sulfur, % dry	0.71–0.89
Particle size, microns	4.0 mean; 95% <15

Table 2.2 shows a comparison of particulate, SO₂, and NO_x emissions from a coal diesel engine and a conventional diesel engine when operating at full load. The total particulate emission level for the coal diesel is between 15 and over 20 times the conventional diesel level. The increase in particulates results from the presence of noncombustible ash in the fuel and the incomplete burning of the coal during the combustion process. The SO₂ emission level is double the conventional diesel level. This value is based on coal containing 1% sulfur by weight. The SO₂ emission level will vary directly with the sulfur content of the fuel. The NO_x emission level of the coal-diesel is between 45% and 65% of the conventional diesel level. The water in the fuel acts to suppress NO_x formation during combustion. However, there is still substantial NO_x generation from the presence of fuel-bound nitrogen in the CWS.

Table 2.2 Comparison of Conventional and Coal Slurry Diesel Emissions at Full Load (3000 hp)

	Conventional	Coal
Particulates Unburned Carbon Ash	2 lb/hr	15–30 lb/hr 15 lb hr
SO ₂	10 lb/hr 130 ppmv	20–30 lb/hr 250–350 ppmv
NO _x	38 lb/hr 1100 ppmv	18–25 lb/hr 500–700 ppmv

Any emissions control strategy must include a means for reducing particulate emissions. The testing and evaluation of particulate collection devices have been carried out by GEESI. Among the options they have considered are high-temperature metal and ceramic filters, granular beds, and cyclones.

The investigation of SO_2 and NO_x control methods was undertaken primarily at GE-CRD. To reduce SO_2 emissions to the level of a conventional diesel, three classes of SO_2 sorbents were tested: (1) copper oxide supported on inert substrates, (2) sodium bicarbonate, (3) and calcium-based sorbents. Sodium bicarbonate and calcium-based sorbents are disposable. Copper oxide is a regenerable SO_2 sorbent and also acts as a NO_x reduction catalyst when ammonia (NH_3) is injected. Laboratory tests were performed to evaluate all three classes of sorbents for SO_2 removal and the copper oxide sorbent for NO_x removal.

Section 3

REGENERABLE COPPER OXIDE SORBENTS

3.1 BACKGROUND

Copper oxide supported on alumina ($\text{CuO}/\text{Al}_2\text{O}_3$) has the potential to be part of an integrated emissions control system for coal-fueled diesel engines. With the inclusion of a suitable particulate removal device, SO_2 , NO_x , and particulates can all be removed from engine exhaust. One motivation for looking at copper oxide is that it is a regenerable SO_2 sorbent. Copper oxide reacts with SO_2 as follows:

After the CuO is converted to copper sulfate, the sorbent is regenerated by flowing a reducing gas, such as methane, over it. With methane the reaction is:

The copper is then reoxidized when it comes in contact with the exhaust gas:

Copper oxide is highly reactive as a sorbent in the temperature range of the exhaust gases as they exit the turbocharger at full load, approximately 700–800 °F.

Copper oxide and copper sulfate also act as NO_x reduction catalysts with the injection of ammonia. Copper sulfate is the more effective catalyst. Some possible reactions for this NO_x reduction include:

UOP, Inc. and DOE Pittsburgh Energy Technology Center have both examined CuO supported on Al_2O_3 for SO_2 and NO_x removal from utility boilers. Exhaust from such a source contains SO_2 concentrations in the range of 2000–3000 ppmv, an order of magnitude greater than in the coal diesel exhaust. They used a fluidized bed absorber with 1-to 2-mm pellets containing 7% Cu by weight. Their results showed that 90% SO_2 removal and 90% NO_x reduction are achievable.^{1,2}

At GE-CRD two main questions were addressed in the bench-scale testing of CuO: Would CuO be an effective sorbent for SO_2 concentrations in the range of 300 ppmv? In what type of process should the CuO be used?

Because of the limited space on the locomotive, the prospect of using CuO on board presents a logistical problem. The space allocated for emissions control is a volume 7 ft wide, 7 ft high, and 10 ft long. The impracticality of using a fluidized bed led to the search for an alternative process. The first process considered was the use of CuO-supported pellets in a fixed granular bed. Testing by GEESI had shown that a granular bed may have the potential to be one component of a particulate cleanup system that includes cyclones located upstream of the turbocharger. This process showed encouraging results in bench-scale experiments and was scaled up to run with exhaust from a single-cylinder diesel engine.

During the scale-up of the granular bed, another process for using CuO sorbent was conceived — injection of $\text{CuO}/\text{Al}_2\text{O}_3$ powder into the engine exhaust duct. This process would entail the use of high-temperature metal or ceramic filters to capture both the sorbent and exhaust particulates. The filters would be housed in the emissions control area. Comparison of bench-scale test results indicated that the powder injection process was superior to the granular bed process.

Nevertheless, the diesel engine granular bed test was performed because of its advanced stage of development. The final stage of testing involved scaling up the powder injection process to run on the diesel engine.

3.2 CuO-SUPPORTED PELLETS

3.2.1 Bench-Scale Tests on CuO-Supported Pellets

The bench-scale tests were designed to investigate the reactivity and durability of various CuO pellets in fixed bed adsorption. The tests examined what fraction of a 300-ppmv SO₂ stream could be removed, and what sorbent composition should be used. In an effort to reduce the size of a full-scale granular bed, sorbents with high copper contents were tested initially. The use of such a sorbent would reduce the amount of unreactive substrate material in the pellet and thus reduce the overall weight and volume of the bed.

A schematic of the experimental test system is shown in Figure 3-1. A 6-inch-deep bed of pellets was supported in a 1-inch-wide stainless steel reactor. The gas mixture components were metered through rotameters and flowed through heated lines before entering the reactor. The inlet and exit temperatures of the reactor were controlled to maintain a constant bed temperature. The gas composition was nominally 300 ppmv SO₂, 13% O₂, 6% CO₂, and the balance N₂. These are the approximate values found in the coal locomotive exhaust. The inlet concentrations were measured through a bypass line at the beginning of each run and periodically during the run. The SO₂ concentration at the exit was measured continuously throughout the test. A DuPont 400 Photometric Analyzer was used to measure SO₂ concentration. After each run, the pellets were regenerated with CH₄. The SO₂ analyzer was also used to determine the end of regeneration.

Tests were performed on the three pellet types listed in Table 3.1. The sorbent on a ZnO/Al₂O₃ substrate and the sorbent on an SiO₂ substrate were tested under similar operating conditions of 800 °F bed temperature and a superficial velocity of 1 ft/s. The superficial velocity

represents the average gas velocity through the reactor if no pellets were present.

Table 3.1 Copper Oxide Sorbent Pellets

Supplier	Cu (%)	Substrate	Surface Area (m ² /g)
United Catalyst, Inc.	34	ZnO/Al ₂ O ₃	80
United Catalyst, Inc.	26	SiO ₂	55
DOE Pittsburgh Energy Technology Center	5.6	gamma alumina	150

Figure 3-2 shows the changes in SO₂ removal efficiency with time for two runs using sorbent on a ZnO/Al₂O₃ substrate. With an inlet concentration of 430 ppmv, this sorbent was initially extremely effective at adsorbing SO₂. The SO₂ adsorption capacity of the sorbent greatly increased during the second run, with 76% of the available copper being utilized. This increase was caused by fissuring of the pellets, however, which increased their effective surface area. After two runs the pellets started to crumble, resulting in an unacceptable attrition rate. Figure 3-3, for the first run with the SiO₂ substrate, shows adsorption characteristics similar to those obtained in the first run with the ZnO/Al₂O₃ substrate. About 30% of available copper was utilized. However, the SiO₂ sorbent also fissured after two runs.

Pollack et al. postulated that the disintegration of the pellets results from the presence of crystalline CuO in the pellet.³ During the adsorption cycles, the crystalline CuO expands into CuSO₄; during the regeneration and oxidation cycles, it contracts back to CuO. These processes physically stress the pellet so that it breaks apart. The high percentage of Cu in the pellets is responsible for the presence of crystalline CuO. Pollack et al. found that in alumina pellets with low Cu content and high surface area (such as the gamma alumina sorbent), the Cu exists not as crystalline CuO but in an extremely thin layer in a noncrystalline form. This noncrystalline form is able to withstand the cycling of the adsorption and regeneration processes without propagating cracks through the substrate.

The CuO sorbent on a gamma alumina substrate proved more durable than the other two. After four runs, there was less than 1% total attrition. The sorbent was also put through a set of parametric tests to see how it performed under various operating conditions. The temperature of the gas was varied over a range of 700–900 °F and the velocity was varied over a range of 0.5–2.0 ft/s.

Figure 3-4 shows the results of temperature variation. The adsorption of SO₂ increases as the temperature increases. As the reaction temperature is lowered from 800 °F to 700 °F, SO₂ removal efficiency decreases. Subsequent increases to 800 °F and 900 °F show corresponding increases in efficiency.

Figure 3-5 shows the results of varying the velocity through the reactor. The SO₂ removal efficiency increases as velocity through the reactor decreases. This variation occurs because of the increased residence time of the gas in the bed at lower velocities. Adsorption decreases more slowly at the lower velocities.

Figure 3-6 shows a run in which the bed was taken to near saturation. Conditions were 800 °F and 1.0 ft/s. The plot shows that greater than 90% SO₂ removal was achieved for 7 hours. At 10 hours, where instantaneous removal has dropped to 75%, the overall sulfur capture for the run is 90%, with 33% of the available Cu being utilized. At 15 hours, when instantaneous removal has dropped to 20%, the overall sulfur capture is 73% and the Cu utilization is 53%. Overall utilization of the Cu is limited by the plugging of pores within the pellet, which makes some of the internal CuO unavailable as the adsorption progresses.

Results of the tests with the gamma alumina sorbent suggest that pellets with reduced Cu content may be suitable for SO₂ capture in a granular bed. From the data shown in Figure 3-6, the sulfur capacity of the sorbent, and hence the size of a full-scale bed, *can be estimated*. Based on a typical locomotive trip that would use 5000 gallons of CWS with 1% sulfur in the coal, the locomotive would be carrying 250 lbs of sulfur per run. The exact amount of sorbent required

would depend upon the goal for overall sulfur capture as well as on the process variables.

Seventy-three percent total sulfur removal was achieved with 53% of the available Cu being utilized. At this level of total sulfur capture, the Cu/S ratio is equal to 1.9/1. As defined here,

$$\frac{\text{Cu}}{\text{S}} = \frac{\text{moles available Cu}}{\text{moles S captured}} = \frac{1}{0.53} = 1.9$$

This ratio will change as the total sulfur capture changes. Scaling this result from the bench-scale test to 73% capture of the 250 lbs sulfur on board the locomotive, 685 lbs of Cu would be required. For the 5.6% Cu pellet tested, 12,250 lbs of sorbent would be required. Based on a bulk density of 37.5 lbs/ft³, the total volume of sorbent required would be 325 ft³. This volume is equivalent to two-thirds of the available space. If a granular bed were to be used, however, it is probable that the Cu content would be between 7% and 10%. UOP has carried out their testing with a 7% Cu pellet. Test results obtained by Yeh et al. suggest that 10% Cu is close to the upper limit without unacceptable attrition.² Assuming a pellet with 7% Cu, the 685 lbs of Cu would require only 9760 lbs of sorbent. The volume of this quantity of sorbent is 260 ft³, which would occupy roughly half the volume available in the emissions control area of the locomotive.

Based on the engine flowrate of 18,000 ACFM at full load, 300 ft² of bed frontal area would be needed to maintain a velocity of 1 ft/s. The granular bed would have to consist of multiple thin beds stacked together, for example, six layers of 50 ft² each. The 300 ft² of frontal area coupled with the sorbent volume of 260 ft³ results in a bed depth of 10 inches, which is 4 inches deeper than the bench-scale test bed from which the sorbent capacity was obtained. The increased depth would result in higher SO₂ removal, but also higher bed pressure drop. A possible alternative would be to decrease the bed depth and increase the frontal area, thereby maintaining the same sorbent volume. Although these calculations are only estimates, they show that fitting a granular bed of sufficient capacity on the locomotive is a possibility that should receive further consideration.

3.2.2 Diesel Engine Tests on CuO-Supported Pellets

The diesel engine tests with CuO pellets had two primary goals. One was to get a more accurate idea of the sulfur capacity by using a scaled-up granular bed. The other was to test the NO_x removal capabilities of CuO with NH₃ injection.

A single-cylinder Yanmar diesel engine was used to create the exhaust that was run through the granular bed. Although the engine was run on diesel fuel, not CWS, it provides gaseous emissions close to the values that were measured on a coal-fired diesel at GETS. On diesel fuel the Yanmar engine produced 500–600 ppmv NO_x and 135 ppmv SO₂. The SO₂ concentration was lower than that from a coal diesel but could be augmented by doping the diesel fuel with liquid carbon disulfide (CS₂). The CS₂ burns to produce SO₂ and CO₂.

A schematic of the setup is shown in Figure 3-7. The Yanmar is a single-cylinder engine with a 4-inch stroke and 4-inch bore. The engine was run at 12 hp and 2000 rpm and had a nominal flowrate of 60 ACFM at 750 °F. The granular bed was 13.5 inches in diameter and 9 inches deep. (This value was chosen based on the bed size estimate given at the end of Section 3.2.1.) These dimensions give the bed a volume 350 times that used in the bench-scale tests. The velocity through the bed is approximately the same as in the bench-scale tests, that is, 1 ft/s. However, because the bed was one and a half times the depth of the bench-scale bed, the residence time was 50% longer.

The sorbent used in this test was purchased from UCI and contained 12% Cu by weight. Although the Cu percentage is slightly above the 10% value recommended by Yeh et al.² (cited in Section 3.2.1), the sorbent was chosen primarily because of its availability in the quantity needed. The exhaust from the engine is fed to the top of the granular bed by a 3-inch duct. Inlet concentrations of SO₂ and NO_x are measured in the duct just before it connects to the bed. Ammonia is injected about 4 feet upstream of the bed to allow it to mix with the inlet gas. The analyzers used for gas concentration measurements are a Beckman 755 for NO_x and a DuPont

400 Photometric Analyzer for SO₂.

Figures 3-8a through c show SO₂ removal during three periods of the Yanmar engine test. Initially, as shown in Figure 3-8a, the SO₂ concentration was 135 ppmv. The fuel was not doped with CS₂. At 180 minutes the SO₂ was increased to 195 ppmv. Through the first 430 minutes of testing, the SO₂ removal was 93% or greater. Shortly after this point, the SO₂ removal began to decrease and continued decreasing over the next 200 minutes. Initially, this decrease was thought to be caused by the decreasing reactivity of the sorbent. However, inspection of the granular bed at this point revealed that the bed support had broken and the sorbent pellets were gradually spilling through into the exhaust duct. About 40% of the sorbent had fallen through and was reloaded into the bed after the support was repaired.

As shown in Figure 3-8b, the test was resumed with the SO₂ inlet concentration increased to 300 ppmv, the value in the coal-diesel exhaust. For the next 200 minutes, the SO₂ removal was consistently greater than 95%.

At this point, because of time constraints, the decision was made to increase the SO₂ concentration significantly in order to speed up the sulfation of the bed. It was thought that a measure of bed sulfur capacity could still be obtained in this way. An increase in the SO₂ to 895 ppm resulted in a drop in capture from 95% to 87%. Capture then started to decline gradually over the next 400 minutes to about 70%. The temporary increase in removal efficiency seen at 1100 minutes was a result of a higher bed temperature, about 825 °F, during that particular run segment. As shown in Figure 3-8c, at 1300 minutes the SO₂ concentration was increased to 1220 ppmv to further speed up the sulfation. Over the next 450 minutes, the SO₂ removal efficiency continued to decline steadily from 70% to 36% at the end of 29 hours of testing.

Over the entire Yanmar engine run, 70% overall sulfur capture was achieved with 63% Cu utilization. On the bench-scale test, 73% overall capture was achieved but only with 53% Cu

utilization. The high degree of Cu utilization in the Yanmar test shows that less sorbent was required for nearly the same amount of total sulfur capture as in the bench-scale test. The Cu/S ratio for the Yanmar engine test was 1.6/1, compared to 1.9/1 for the bench-scale tests. This result suggests that a smaller bed size would suffice than was previously estimated from the bench-scale results. The deeper bed and longer residence time are probably major contributing factors to the reduced Cu/S ratio. The artificially high SO₂ concentration, on the other hand, may have acted to increase the Cu/S ratio. Although not conclusive, this effect is suggested by the drop in instantaneous removal efficiency that occurred when the SO₂ concentration was increased from 300 ppmv to 895 ppmv. If correct, this conclusion implies that an actual system with lower SO₂ concentrations may have a Cu/S ratio even lower than 1.6/1. It should also be noted that the different Cu content of the sorbent adds uncertainty to the comparison with the bench-scale results. It is not clear whether changing the Cu content would increase or decrease the Cu utilization.

Following an analysis similar to the bench-scale test, a bed size estimate was made for the 12% Cu sorbent based on a Cu/S ratio of 1.6/1 and 70% overall sulfur capture. For the 12% pellet, the estimate results in a 4650 lbs sorbent having a volume of 125 ft³. Assuming a 7% pellet at the same Cu utilization, a bed volume of 220 ft³ is estimated, which is about 15% less than the bench-scale estimate. Although based on limited data, these numbers suggest that there would be sufficient space on the locomotive to fit a granular bed.

The Yanmar engine test presented the first opportunity to look at NO_x reduction in the presence of NH₃ injection. Four of the possible reactions between NO_x and NH₃, listed in Section 3.1, are considered here:

In general NO_2 comprises less than 10% of total NO_x . Measurements of NO and NO_x confirmed that NO did comprise greater than 90% of the NO_x . Thus Reactions 3.9 and 3.11 do not make a large contribution to NO_x reduction. It is not clear whether Reaction 3.8 or 3.10 contributes more to NO reduction. It should be noted, however, that the stoichiometric ratio of NH_3 to NO is different for the two reactions. In Reaction 3.8 the ratio is 1/1; in Reaction 3.10 it is 2/3.

The results of NO_x reduction from NH_3 injection are shown in Figures 3-9a and b. Shown in the plots are fractional NO_x removal (dotted line) and NH_3/NO_x ratio (solid line). The NH_3/NO_x ratio is defined as a molar ratio. The NO_x removal is shown fractionally (instead of as a percentage) so that comparisons can be made on the same scale between NO_x removal and NH_3/NO_x ratio.

The data in these figures indicates that significant NO_x removal can be achieved with NH_3 injection. The trend in NO_x removal tracks the change in NH_3/NO_x ratio. As NH_3/NO_x increases, NO_x removal increases; as NH_3/NO_x decreases, NO_x removal decreases. More significant, however, is the way the relative values of NH_3/NO_x and fractional NO_x removal shift over time. As shown in Figure 3-9a, initially the value of NH_3/NO_x is higher than the fractional NO_x removal. Based on reactions 3.8 and 3.10, this result indicates that all of the ammonia is not being utilized. Over time the NH_3/NO_x ratio decreases for a given level of NO_x removal. From 200 to 680 minutes, the values of NH_3/NO_x and fractional NO_x removal are approximately equal. After that the value of NH_3/NO_x becomes lower than the fractional NO_x removal.

This relation between NO_x removal and NH_3/NO_x ratio is not unexpected given what is known of the catalytic properties of copper oxide and copper sulfate. While both CuO and CuSO_4

act as NO_x reduction catalysts in the presence of NH_3 , CuSO_4 is the more effective. Therefore the NO_x reduction reaction is most inefficient when the bed is initially low in CuSO_4 . As the bed becomes more and more sulfated, the catalytic activity of the bed increases, increasing the amount of NO_x removal for a given level of NH_3/NO_x .

As shown in Figure 3-9b, the fact that the NH_3/NO_x ratio becomes lower than the fractional NO_x removal suggests that Reaction 3.10 is taking place. Based on stoichiometry, this is the only reaction for which the value of fractional NO_x removal can be higher than the experimental NH_3/NO_x ratio. For all the other reactions, even if 100% NH_3 utilization occurs, the NH_3/NO_x ratio could never be less than the fractional NO_x removal.

Although it seems that a CuO granular bed could be viable for sulfur capture, other considerations point to drawbacks of a granular bed. The biggest difficulty is how to integrate a particulate cleanup device with a granular bed. In tests on the single-cylinder coal diesel engine in Erie, GEESI examined several options for particulate removal. Two options incorporated a granular bed both for particulate removal and for SO_2 removal. One option used cyclones upstream of the turbocharger followed by a granular bed downstream of the turbocharger. The cyclones would be for coarse particulate removal and the granular bed for fine particulate and SO_2 removal. The other option used only a granular bed downstream of the turbocharger so that the granular bed would receive the full particulate loading as well as scrub SO_2 .

GEESI's testing showed that the option without the cyclones was not viable. Because a granular bed cannot be cleaned on-line as conventional filters can, the bed must be capable of sustaining an acceptable pressure drop for the duration of the trip without being cleaned. GEESI's test results showed that this goal is not possible with reasonable bed depths and gas velocities. The option with cyclones upstream of the turbocharger could be viable for emissions removal, but is not acceptable because of its effect on engine performance. The cyclone location exacts too large a penalty in turbocharger efficiency.

3.3 CuO/Al₂O₃ POWDER

3.3.1 Bench-Scale Tests on CuO/Al₂O₃ Powder

The motivation for looking at CuO supported on alumina powder was to develop a simpler integrated emissions process than could be achieved with a CuO granular bed. While a CuO granular bed can be very effective for SO₂ and NO_x removal from the diesel exhaust, additional particulate cleanup devices such as cyclones are necessary. However, injecting CuO/Al₂O₃ powder into the exhaust followed by a particulate filter can eliminate the need for a large reactor vessel. The CuO/Al₂O₃ would be captured along with exhaust particulates on the filters. SO₂ capture would occur both in the gas stream and in the filter cake that forms. Selecting the minimum alumina particle size to be larger than the maximum ash size (about 10 microns) makes it possible to separate the two fractions later. The recovered CuO can then be regenerated.

To investigate the effectiveness of CuO powder for SO₂ removal, a 300 ppmv SO₂ stream was passed through thin layers of powder under various conditions. The thin powder layers approximate the accumulation of powder on a filter element after injection into the exhaust. The powder was supported on a 2-inch diameter filter disc of sintered Inconel fiber. The disc was held in a heated reactor. The outlet stream was monitored continuously for SO₂ concentration with a DuPont 400 Photometric Analyzer. The operating conditions were varied over a wide range of values: powder thickness, 1–5 mm; gas temperature, 500–800 °F; gas velocity, 5–15 ft/min.

The sorbent was prepared by wet impregnation of Aldrich gamma alumina in a 20% solution of copper nitrate hemipentahydrate. The size of the powder ranged from 30 to 100 microns. The sorbent was dried and then calcined in air at 650 °C for 4 hours. The prepared sorbent contained 4.5% Cu by weight.

In general the adsorptions were carried out until removal efficiency fell to about 50% (150 ppmv outlet SO₂). The tests run with powder were much shorter than the pellet tests. While

a granular bed must have enough capacity for an entire locomotive trip, the powder needs only enough capacity for the interval between pulse cleanings of the filters, which is on the order of 15 to 30 minutes.

Figure 3-10 shows the effect of temperature on SO_2 removal in a 5-mm powder layer with a gas velocity of 10 ft/min. The results indicate that the powder is more reactive at lower temperatures than the pellets. At 500 °F, greater than 90% removal was achieved for 9 minutes and greater than 50% for 27 minutes. At 600 °F, greater than 90% removal was achieved for 35 minutes. With pellets, very poor SO_2 removal would be expected at these temperatures.

In a test in which the adsorption was run to completion, the Cu utilization of the powder was found to be much higher than that of pellets. When instantaneous SO_2 removal dropped below 5%, over 90% Cu utilization in the powder layer had been obtained. As shown in Figure 3-6, for gamma alumina pellets only 53% Cu utilization was obtained when instantaneous SO_2 removal dropped below 20%. This comparison shows that for powder, a greater amount of the available copper can be utilized. Less total sorbent is, therefore, required for powder than for pellets.

Figures 3-11 through 3-13 show the effect of layer thickness and face velocity on SO_2 removal. Each plot shows removal for a single thickness at various velocities. The temperature is 700 °F for all runs. As expected, the SO_2 removal efficiency improves with increasing thickness and with decreasing velocity. Figure 3-11 shows that for the thickest layer, 5-mm, 100% SO_2 capture was achieved for at least 30 minutes at all velocities. In Figure 3-12, for the 2.5-mm layer at 15 ft/min, greater than 90% removal is achieved for 14 minutes and greater than 50% removal for 34 minutes. In Figure 3-13 for the 1-mm layer at 10 ft/min, greater than 90% was attained for 20 minutes and greater than 50% removal for 36 minutes. These adsorption times fall within the desired range for use with a bag or candle filter. In an actual system with powder injection, the SO_2 removal is expected to be augmented by additional reaction that occurs during entrainment in the exhaust duct. Even at the least favorable sets of conditions, the degree of SO_2 removal looks

promising.

The CuO/Al₂O₃ powder concept was further tested at GETS in Erie. In these tests coal diesel exhaust was run through a candle filter that was precoated with 1 to 2 mm of sorbent. Greater than 90% SO₂ removal was achieved for up to 25 minutes.

The use of CuO-coated alumina powder looks very promising as a means of removing SO₂ from exhaust gas streams. The powder has greater capacity and is reactive at lower temperatures than CuO pellets. The time periods over which the sorbent stays reactive are sufficient to last through a filter cleaning cycle.

3.3.2 Diesel Engine Tests on CuO/Al₂O₃ Powder

The favorable results with CuO powder led to further development of a process for using this sorbent. As conceived, such a process would use CuO, a regenerable sorbent, in the simultaneous removal of SO₂, NO_x, and particulates. The sorbent would be injected into the engine exhaust duct upstream of particulate filters. The SO₂ removal would occur both as the sorbent was entrained in the duct and as the gas passed through the sorbent cake that formed on the filters. At the same time, NH₃ would be injected into the exhaust duct for catalytic NO_x reduction. The sorbent and the exhaust particulates would be captured on the filters. Selecting the sorbent size to be larger than the exhaust particulates makes it possible to separate the two fractions later. The particulates in the coal diesel exhaust are generally less than 10 microns; the sorbent is sized to be 20–100 microns. The exhaust particulates are disposed of while the sorbent is regenerated. The separation and regeneration steps would occur off the locomotive.

To test the feasibility of this concept, a candle filter vessel was designed for use with the Yanmar engine. The primary purpose of this testing was to examine the gas phase cleanup, that is, SO₂ and NO_x removal. The filter type and the particulate removal process were not optimized in this test for two reasons: (1) While the gaseous components of the Yanmar engine exhaust can be

made similar to coal diesel exhaust, the particulates from this engine are different. The coal diesel particulates contain mainly noncombustible ash, while the Yanmar engine particulates are diesel soot, which has very different physical characteristics. (2) The candle filters used in the test are not the ones that GEESI has recommended for use on the locomotive. GEESI has proposed to use envelope filters that were designed and tested at GEESI. Candle filters were chosen in this test for simplicity and interchangeability.

A schematic of the test assembly is shown in Figure 3-14. The sorbent and NH_3 were injected into the exhaust duct just downstream of the engine. The 11-ft duct length provided a residence time of approximately 500 ms for in-duct reaction to occur between the sorbent and SO_2 . The sorbent was then captured on the candle filter, where SO_2 removal continued to occur through the filter cake. The position of the candle filters is shown schematically.

Figure 3-15 shows a top view of the actual position of all the filters in the vessel. The vessel has three rows of filters that can hold a total of ten filters; the middle row holds four and the outer rows hold three each. Each row is connected to the pulse cleaning tank through a solenoid valve. A pulse controller continuously monitors the pressure drop across the candle filters. When the pressure drop exceeds a preset level, the controller opens one of the solenoids causing the corresponding row of filters to be pulse cleaned with a blast of air. Each time the pressure drop setpoint is exceeded, the next solenoid is opened, cleaning the next row of filters. By cleaning only one row at a time, two-thirds of the total filter cake is retained enabling SO_2 removal to be sustained.

Several issues were addressed in this test. Of primary importance was how to form a suitable filter cake in order to achieve high SO_2 removal. Other issues included the effect of sorbent injection rate on SO_2 removal, the relation between NO_x removal and NH_3 injection rate, and the effect of pressure drop and pulsing on performance.

The sorbent was prepared by the process described in Section 3.3.1 for the bench-scale

powder tests. For the Yanmar engine test, however, the copper concentration was increased to about 8% Cu by weight from 4.5%. The sorbent was injected into the exhaust duct using a Miller Thermal 1250 Roto-Feed Powder Hopper. The candle filters were purchased from Fluid Dynamics. They were manufactured out of a sintered stainless steel fiber and were initially 2 ft long and 2 inches in diameter. At later stages in testing, 1.5-ft filters were used. The total surface area for the ten 2-ft filters was 10.46 ft². Before each run began, the filters were precoated with 60 grams of sorbent primarily to protect them against blinding by the diesel soot.

Five tests were run with sorbent injection in the candle filter vessel. As the tests progressed, the system was continually refined. Data is presented for Tests 3 through 5. In Test 1, the highest SO₂ removal achieved was less than 40%. After the test, inspection of the inside of the filter vessel showed very little cake forming on the filters. The inability to form a cake resulted from poor distribution of the sorbent as it entered the filter vessel. Most of the sorbent was falling into the hopper rather than adhering to the filters.

To improve dispersion of the sorbent as it entered the vessel, a flow distributor was designed. The distributor was placed in the top of the vessel where the exhaust entered. In Test 2, the distributor did increase the maximum SO₂ removal to 60%. However, inspection of the vessel again showed poor cake formation on the filters.

Before Test 3 (data shown in Figures 3-16a through c), two significant changes were made in order to further improve the filter cake formation. The first change was to increase the velocity of the gas passing through the filters. This velocity, or Air/Cloth (A/C) ratio, is equal to the total volume flow of gas divided by the total filter area. A higher A/C ratio would hold the sorbent particles on the filter better. The A/C ratio was increased by reducing total filter surface area by 25%. The 2-ft filters were replaced by 1.5-ft filters. The second change was to classify the sorbent to remove the fraction of particles greater than 150 mesh (104 microns). Particle size distributions were measured at GEESI both before and after the large-particle fraction was removed. Before

classifying, more than 50% of the mass was in particles larger than 150 mesh. After classifying, less than 3% of the mass was in particles larger than 150 mesh. Removing the large particles caused a greater amount of sorbent to adhere to the filter. In addition the smaller particles are potentially more reactive.

Test 3 showed marked improvement in performance over the previous two. Figures 3-16a through c show filter pressure drop, SO₂ removal, and NO_x removal, respectively. The pressure drop data shows that the filter was continuously building up a cake. After the fourth pulse, because the pulse period had gotten too short, the pulse setpoint was increased from 20" to 30" H₂O. The decrease in the rate of pressure rise, seen on the fifth cycle, was due to the powder feeder being temporarily turned off from 164 to 178 minutes. The powder feeder ran out of powder at 198 minutes.

The data in Figures 3-16a and b indicate that SO₂ removal varies with filter pressure drop. As a thicker cake forms, the result is not only higher pressure drop but also increased SO₂ removal efficiency. When the filters are pulsed, there is a step decrease in removal efficiency as one bank of filters is cleaned. Because of the reduced pressure drop on that filter bank, the cake quickly reforms there and restores the higher SO₂ removal.

The data in Figure 3-16b indicates that increases in the powder injection rate have an effect on the SO₂ removal curve. This effect can be seen, for example, at 112 and 120 minutes, where there is a sharp increase in the slope of the SO₂ removal curve. The sorbent injection rate was increased further at 130, 141, 160, 186, 190, and 195 minutes. Because of problems with the powder feeder, absolute sorbent feed rates could not be measured; hence Cu/S ratios could not be calculated for this test.

As the injection rate was increased, the removal efficiency continued to increase up to 85% at 164 minutes, at which point the sorbent feeder was turned off. The removal efficiency steadily decreased as the sorbent in the filter cake was exhausted. At 178 minutes, the feeder was turned

back on. The sharp increase in efficiency at this point can be used to estimate the magnitude of removal occurring in the duct. Assuming that the near step-change in efficiency results from SO_2 capture in the duct, 25 to 30% of removal appears to be occurring in the duct. The filter was pulsed at 180 minutes, after which the efficiency again started to increase. It should be noted that higher feed rates were required to approach 85% removal efficiency this time because the sorbent in the filter cake was spent during the time that the feeder was turned off.

The filters were pulsed at 196 minutes; at 198 minutes the feeder ran out of powder. It is very likely that SO_2 removal efficiencies greater than 90% could have been achieved had more sorbent been available to continue the run. The main problem in this run involved the inability to measure absolute sorbent feed rate and hence, Cu/S ratio.

Figure 3-16c shows that significant NO_x removal is achievable by using the candle filters. Greater than 90% NO_x removal efficiency was obtained in this test. The ammonia injection was started at 142 minutes and resulted in a sharp increase in NO_x removal. The NO_x removal as a function of pressure drop showed a trend similar to SO_2 . As seen in the spikes at 147, 182 and 196 minutes, NO_x removal increases with pressure drop and then sharply decreases during the pulse cleaning.

From 160 to 180 minutes, NO_x removal leveled off at 70%. From 180 to 195 minutes, the NH_3 injection rate was gradually increased approximately 50% and then held constant. As with the powder feeder, there was a problem in this run with measuring the ammonia flowrate. Therefore NH_3/NO_x ratios could not be included in this plot. At the higher NH_3 feed rate, the NO_x removal efficiency appeared to level off at a value of 95%. After the last pulse at 196 minutes, the NO_x removal continued to increase even though the powder feeder was then turned off and the NH_3 held constant. The NO_x removal continues to occur through the CuSO_4 in the filter cake, even without sorbent injection.

The primary goal in Test 4 was to obtain an accurate measure of the NH_3 and sorbent feed

rates. The filter pressure drop, SO_2 removal, and NO_x removal for Test 4 are shown in Figures 3-17a through c, respectively. The filter arrangement was changed for this test. The ten 1.5-ft filters were replaced with seven 2-ft filters. The three other filter connections were plugged. The 2-ft filters were made of a coarser filter medium. Thus although the total surface area was nearly constant, the rate at which the pressure drop increased was expected to be lower. Figure 3-17a confirms this expectation, showing that the rate of pressure drop increase for Test 4 is less than for Test 3.

Figure 3-17b shows SO_2 removal efficiency plotted with Cu/S ratio. At the initial Cu/S ratio of 2.5, the SO_2 removal appeared to be approaching a value in the range of 60%. The sorbent injection rate was increased, however, before the removal efficiency had completely leveled off. At a Cu/S ratio of 3/1, the SO_2 removal was about 80%. At the highest Cu/S ratio of 3.3/1, SO_2 capture greater than 95% was consistently achieved. On pulsing, this value dropped to 70–75% and then started increasing again. A Cu/S ratio of 3.3/1 corresponds to only 30% utilization of the available sorbent.

Figure 3-17c shows the variation of NO_x removal with NH_3/NO_x ratio. Once again NO_x removal is shown as a fraction rather than a percentage for easier comparison with NH_3/NO_x ratio. The increase in NO_x removal is seen to follow the increase in NH_3/NO_x ratio. The maximum NO_x removal achieved was 0.86 at an NH_3/NO_x ratio of 0.99. In Test 4 the value of NH_3/NO_x is consistently 0.1–0.15 greater than the value of fractional NO_x removal. Although no direct NH_3 measurements were made in this run, this difference suggests that some NH_3 breakthrough was occurring.

In Test 5, the final CuO test, an effort was made to reduce the Cu/S and NH_3/NO_x ratios for given levels of SO_2 and NO_x capture. Two modifications were made in the test: (1) The gas temperature in the filter vessel was increased 50 °F to roughly 800 °F since bench-scale tests showed that this temperature increase should improve SO_2 capture. (2) A batch of finer sorbent

was injected. The mass median diameter of the sorbent in Test 5 was 25 microns, compared to 45 microns in all the previous runs. A smaller particle size, which would increase the surface area, was expected to result in a more reactive sorbent. The reduction in particle size was also expected to improve the adherence of the sorbent to the filters.

The pressure drop, SO_2 removal, and NO_x removal for Test 5 are shown in Figures 3-18a through c, respectively. The rate of pressure drop increase, shown in Figure 3-18a, was noticeably higher than in Test 4, possibly as a result of the smaller particle size.

Improved SO_2 removal can be seen in Figure 3-18b. Higher removal efficiencies were recorded at Cu/S ratios lower than those in Test 4. Up to 98% SO_2 removal was achieved at a Cu/S ratio of 2.5/1. This ratio is equivalent to 39% sorbent utilization, compared to 30% in Test 4. Although this sorbent utilization is not as high as expected, there is reason to believe that a number of improvements could be made: (1) The filtering system (filter type, filter media, and gas manifolding) could be improved to enable thicker filter cakes to build up for a given pressure drop. As shown in the bench-scale tests, a thicker cake should increase the removal efficiency of the sorbent. A better gas inlet manifold might also improve the percentage of sorbent that adheres to the filter. (2) A more reactive sorbent could be used. The sorbent was made following a simple recipe for wet impregnation found in the literature. The expertise of a catalyst manufacturer in choosing the carrier alumina and the coating process could improve sorbent reactivity.

Figure 3-18c shows that NO_x removal also improved over Test 4. The difference in value between NH_3/NO_x ratio and fractional NO_x removal was decreased. At both 70 and 190 minutes, the fractional NO_x removal was equal to the NH_3/NO_x ratio with a value of 0.80. At 175 minutes, NO_x removal of 0.88 was obtained at the NH_3/NO_x ratio of 0.90. At 150 minutes, NO_x removal of 0.97 was achieved with NH_3/NO_x equal to 1.03.

Test 5 also included two measurements of unreacted NH_3 in the exhaust. The NH_3 was sampled by bubbling the exhaust gas through three 100-ml flasks of 0.02-M H_2SO_4 . The amount

of NH₃ in solution was then measured with an Orion Model 720A Ion Selective Electrode. The measurements were integrated over a 9-minute period so that enough NH₃ would be captured in solution to be above the electrode detection limit.

The first NH₃ sample was drawn from 168 to 177 minutes, where NO_x removal increased from 0.80 to 0.88 and NH₃/NO_x was 0.88. The NH₃ breakthrough concentration for this point was 26 ppmv, which is equivalent to about 6% of the injected ammonia. The second measurement was taken from 180–189 minutes, where NO_x removal increased from 0.72 to 0.80 and NH₃/NO_x was 0.79. The NH₃ in the exhaust was 12 ppmv, 3% of the injected ammonia. At present it is not known what values for NH₃ breakthrough will be considered acceptable. In the future, NH₃ breakthrough may become an important factor in determining the degree of NO_x removal that can be achieved.

3.4 CuO POWDER REGENERATION TESTS

The SO₂ and NO_x removal step comprises only half of the overall process for utilizing copper oxide. The copper sulfate, CuSO₄, that results from the adsorption process must be regenerated back into CuO to be reused as a sorbent. The regeneration process produces SO₂ as a byproduct. This SO₂ stream is highly concentrated, however, and can be more easily converted into a usable end product than the original dilute streams. The regeneration reaction uses a reducing gas, such as methane, in the following reaction:

With CuO pellets, this reaction is known to proceed at temperatures of 850 °F or higher. If this reaction were 100% efficient, the product stream would contain 40% SO₂ by volume. For large-scale utility applications, such as those investigated by UOP and PETC, the concentrated SO₂ stream would be processed to generate a usable byproduct such as sulfur or sulfuric acid. The scale of the locomotive application is much smaller and would probably make such

conversion processes uneconomical. A more likely alternative would be to capture the concentrated SO_2 in a sorbent such as calcium slurry for disposal. However, this issue has not yet been addressed.

For locomotive applications, the regeneration of the CuO would have to occur off the locomotive. Because of the superior performance of the CuO powder over the pellets in adsorption, regeneration of powder, rather than pellets, became the main focus of attention. Regeneration of the CuO powder entails two steps: the chemical regeneration as given by Reaction 3.12 and the separation of the spent sorbent from the ash. One proposed process would combine both steps into a single operation through the use of a fluidized bed regenerator. The bed would be fluidized with methane to effect the chemical regeneration. At the same time, the fluidization process would act as a particle classifier. The smaller ash particles would be entrained into the flow and captured on a downstream filter, leaving behind the larger sorbent particles.

The facilities for testing this process were not available at GE-CRD. A simpler fixed bed regeneration test was carried out to examine the chemistry of the regeneration reaction. The tests were carried out in a 4-inch-diameter fixed bed reactor. A sintered stainless steel filter disc was used to support the sorbent. The reactor and the inlet lines were heat traced to control the sorbent and gas inlet temperatures. The sorbent contained 8% Cu by weight, as in the Yanmar engine tests (Section 3.3.2). The sorbent was first totally sulfated so that the degree of regeneration and methane utilization could be accurately quantified.

Three regeneration runs were made. In Run 1, the reaction temperature was set to 790 °F. This reaction temperature was 60 °F lower than the minimum temperature given in the literature for pellet regeneration. Because the powder was reactive at lower temperatures than the pellets during adsorption, it was postulated that the powder might also be more reactive at lower temperatures during regeneration. The bed was 1.3 inches high and contained 228 grams of sorbent at 8% Cu by weight. The methane flowrate was 0.5 SCFH, the minimum recommended

value for SO₂ analyzer operation. Maximizing the residence time of the methane in the bed was expected to give the maximum methane utilization.

The methane utilization from the regeneration tests is shown in Figure 3-19. The utilization efficiency is derived from the SO₂ emissions measurements made during the test. The relation between these two quantities can be shown by rewriting Reaction 3.12 to account for incomplete CH₄ utilization:

where η = CH₄ utilization efficiency. (3.13)

From this reaction the relation between η and SO₂ concentration can be shown to be

$$\eta = \frac{[\text{SO}_2]}{2-4[\text{SO}_2]}$$

The regeneration in Run 1 is not very efficient at 790 °F. The peak CH₄ utilization efficiency was only 9%. Unlike adsorption, powder regeneration does not appear to work well at reduced temperatures. In Run 2, the reaction temperature was increased to 900 °F while maintaining the same bed height and methane flowrate. The utilization efficiency increased to 29%, equivalent to an SO₂ concentration of 27%. To improve the methane utilization further, the bed height was increased to 4 inches. In Run 3, a peak efficiency of 66% was reached, resulting in an SO₂ concentration of 36.3%.

Efforts to improve efficiency further were not successful because of limitations in the reactor design. Increases in bed height resulted in excessive pressure that caused the reactor to leak. Attempts to reduce the pressure drop through reduction in flowrate also failed. The gas velocity became so low that uniform heating of the bed could not be maintained.

These tests provide preliminary data on the degree of CH₄ utilization that can be expected in a

real regeneration system. As shown in the following simple example, the cost of methane consumption per locomotive trip is not greatly affected by the regeneration efficiency. If we assume that only 50% CH_4 utilization is achieved and that 100% of the 250 lbs of sulfur in the coal is captured by the sorbent, the CH_4 consumption for total sorbent regeneration would be only 3000 ft^3 . At a cost of \$7 per 1000 ft^3 of natural gas, the total cost would be \$20 per locomotive trip, an insignificant amount. The operational cost of regeneration will probably be affected much more by the cost of sorbent heating and by processing of the SO_2 stream than by the methane utilization efficiency of the process.

Investigation of CuO powder regeneration in a more practical configuration will be carried out by GEESI. They have designed a fluidized bed regenerator that will examine both chemical regeneration with CH_4 and the separation of the sorbent from the ash.

3.5 CONCLUSIONS

Copper oxide supported on alumina was successfully tested in two processes for simultaneous SO_2 and NO_x removal: a CuO pellet granular bed and $\text{CuO}/\text{Al}_2\text{O}_3$ powder injection into the exhaust duct. Powder injection is the more promising of the two. Both processes can reduce gaseous emissions to levels well below the level of a conventional diesel. However, a granular bed process would have problems in simultaneously achieving the necessary particulate removal. The granular bed itself cannot act as the sole particulate removal device because of excessive pressure drop. The addition of other particulate removal devices results in too great a penalty in engine performance.

The powder injection process is capable of simultaneous SO_2 , NO_x , and particulate removal on board the locomotive. Yanmar engine testing demonstrated greater than 95% simultaneous SO_2 and NO_x removal. The use of high-temperature metal filters makes it possible to capture the particulates and sorbent without an excessive penalty in engine performance.

It was observed in the powder injection tests that even with a long entrainment time, most capture occurred through the filter cake. It is therefore necessary to ensure that a good cake is established on the filters. Several important factors were identified to improve the adherence of the sorbent to the filters: (1) even distribution of the exhaust flow as it enters the filter vessel, (2) sufficient A/C ratio (greater than 7.5 ft/min), and (3) well-classified sorbent with the fraction larger than 150 mesh removed.

The regeneration of the CuO powder was tested in a fixed bed reactor. A value of 66% CH₄ utilization was achieved in these tests. Higher values could have been attained except for limitations in the experimental apparatus. Because the amount of methane required for regeneration is so small, however, the cost of CH₄ per trip is not significantly affected by the regeneration efficiency.

Section 4

DISPOSABLE SODIUM BICARBONATE SORBENT

The minimum goal for emissions control in the work described here was to make the coal diesel exhaust at least as clean as conventional diesel exhaust. To achieve this result, only SO₂ and particulate reduction are necessary, not NO_x reduction. Sodium bicarbonate (NaHCO₃ — also called nahcolite) was tested as a disposable sorbent that would be used for SO₂ capture only. As with the CuO powder, the sodium bicarbonate would be injected into the exhaust duct of the engine and captured on a filter. Reaction would take place both in flight and in the filter cake. The chemical reaction between sodium bicarbonate and SO₂ is:

The Na/S stoichiometric ratio is 2/1, while for copper oxide, the stoichiometric Cu/S ratio is 1/1.

The experimental setup for sodium bicarbonate was the same as for the CuO powder injection tests. The Yanmar engine was used to generate the exhaust, and the sorbent was injected with the Miller Thermal 1250 Roto-Feed Powder Hopper. Visual inspection of the sodium bicarbonate under a light microscope showed the particles to be in the 10 to 50 micron range.

Only one test was run with sodium bicarbonate. Figure 4-1 shows the candle filter pressure drop. Powder injection occurred for the first 55 minutes and was then stopped. Three pulses occurred at 51, 53, and 54 minutes and a fourth pulse occurred at 58 minutes. At 109 minutes powder injection began again at 75% of the original feedrate. The pressure drop in this test was less than one half of that for CuO injection. The SO₂ removal, however, was equal to the best results obtained with CuO, as shown in Figure 4-2. The Na/S ratios shown in the figure represent the stoichiometric ratio of Na to S. From Reaction 4.1 it can be seen that the 2/1 stoichiometric ratio is equivalent to a 4/1 molar ratio.

At a stoichiometric ratio of 2/1, 0.97 SO₂ removal was reached, the equivalent of 49% sodium

bicarbonate utilization. After the first three pulse cleanings, the sorbent was stopped and the SO_2 removal dropped off. The sorbent injection was resumed at 109 minutes at an Na/S stoichiometric ratio of 1.5/1. An SO_2 removal of 0.94 was attained although the rate of increase of SO_2 removal was slower than for the Na/S ratio of 2/1. At the 1.5/1 ratio, the sorbent utilization increases to 63%.

Measurements of NO_x emissions were made in this test, both with and without NH_3 injection. In both instances, no reduction in NO_x occurred.

Sodium bicarbonate is a better sorbent for SO_2 capture than copper oxide. A much smaller mass flow of sodium bicarbonate is required to achieve comparable SO_2 capture for two reasons: (1) With sodium bicarbonate, 100% of the sorbent particle is reactive; whereas with copper oxide, only 10% by weight of the sorbent is reactive. (2) There is a higher utilization of NaHCO_3 than $\text{CuO}/\text{Al}_2\text{O}_3$. To achieve 95% SO_2 capture, the mass flow of $\text{CuO}/\text{Al}_2\text{O}_3$ is six to seven times that of sodium bicarbonate. The lower mass flow of sodium bicarbonate not only reduces the weight and volume of sorbent carried on board, but also results in a significant reduction in filter pressure drop. At the same SO_2 capture, pressure drop with NaHCO_3 (10–15" H_2O) was one-half to one-third that measured with $\text{CuO}/\text{Al}_2\text{O}_3$. The reduced pressure drop, in turn, can result in improvements in engine and turbocharger performance.

Section 5

DISPOSABLE CALCIUM-BASED SORBENTS

5.1 BACKGROUND

Calcium-based sorbents are used commercially in wet and dry scrubbers to remove SO_2 from the exhaust of large coal-fired combustion systems. The temperatures at which the removal process takes place are generally below 625 °F, and the residence times are on the order of seconds. Utility boiler operators and manufacturers are currently evaluating other SO_2 removal methods, including injecting dry calcium-based sorbents at temperatures near 2250 °F and 1000 °F to produce calcium sulfate and calcium sulfite, respectively. These studies are being performed in large systems with long residence times.

The exhaust of the coal-fueled diesel is approximately 900 °F at full load. The exhaust system is small and the residence times are short. The gases remain hot for about 20 to 60 ms prior to expansion through the engine's turbocharger. The coal slurry, partially cleaned during the manufacturing process, produces 300 ppmv SO_2 in the exhaust. In general sulfation data does not exist for these conditions. This study was designed to provide such data. In addition tests were done to determine whether SO_2 and calcium sorbents would react with NO_x to form nitrogen.

5.2 EXPERIMENTAL APPARATUS

Sulfation data was obtained in an isothermal, refractory-walled tower reactor located at the University of Utah. The reactor, shown in Figure 5-1, was 118 inches high with a 6.3-inch inside diameter. A natural-gas-fired burner attached at the bottom of the furnace supplied hot combustion products that flowed vertically upward inside the reactor. Independent wall and gas temperature control was provided by two natural gas burners fired downward in annular channels around the main combustion chamber. Suction pyrometers and thermocouples were used for continuous monitoring of gas temperature.

The SO₂ was metered into the inlet natural gas; sorbent was metered by weight loss from a K-tron twin screw feeder, shown in Figure 5-2. The sorbent was pneumatically transported through a water-cooled injector and atomized into the venturi throat located at the bottom of the reaction zone. Injection into the venturi facilitated rapid mixing of SO₂ and sorbent. The dimensions of the venturi throat and sorbent injector are shown in Figure 5-3.

The furnace exhaust was monitored continuously for CO₂ (nondispersive infrared), O₂ (paramagnetic), and SO₂ (nondispersive ultraviolet). The nominal gas concentrations for the tests were 3.4% CO₂ and 16.0% O₂. The SO₂ sample was drawn through a controlled temperature, stainless steel, phase discrimination probe and conditioned with two glass wool filters, an electrically heated line (250 °F), two Perma Pure membrane dryers, and a 60-micron, stainless steel filter.

The sorbents studied included two commercially available hydroxides: an atmospherically slaked lime (Linwood Calcium Hydrate) and a pressure-slaked dolomite (Genstar Pressure-Hydrate Dolomite). Sorbents were characterized by SEM photography, BET surface area, N₂ and Hg porosimetry, and sedigraphy for particle size analysis. Characteristics of the calcium sorbent are listed in Table 5.1.

Table 5.1 Calcium Sorbent Properties

Analysis	Linwood Calcium Hydrate	Genstar Pressure-Hydrate Dolomite
Chemical form	Ca(OH) ₂	CaMg(OH) ₄
BET surface area, m²/g	16.0	20.0
Density, g/cm³	2.3	2.3
Medium size, microns	2.2	1.4

Upon reaching test conditions, the SO₂ concentration in the reactor (without sorbent present) was measured. The sorbent was injected in the reactor at a rate resulting in a Ca/S atomic ratio of

2/1 after recording the baseline data. The SO_2 concentration at various residence times was measured by moving the gas sample probe along the length of the reactor.

5.3 RESULTS

Results from sulfating the sorbent at a number of exhaust temperatures are shown in Figure 5-4. For these tests, 200 ppmv SO_2 was initially present in the exhaust gas. The data shows less Ca utilization (less sulfur capture; 10% calcium utilization equals 20% sulfur capture) with increasing gas temperature. As the temperature is increased above 1000 °F, it is thought that reactive sites within the particle become inaccessible as a result of pore clogging at the particle surface caused by formation of low-density sulfite. At the lower temperatures, 800 to 1000 °F, sulfite kinetics is slower and diffusion into the particle can occur before the pores close. At still lower temperatures, it is likely that the kinetics is too slow to be of practical significance. It should be noted that the thermal sintering (desurfacing process) of the sorbent is unlikely at the temperatures studied. There should therefore be little loss of reactive calcium oxide sites due to this mechanism.

Data presenting calcium utilization as a function of residence time is given in Figure 5-5 for three SO_2 concentrations studied: 200, 500, and 1000 ppmv (dry). These results are not unexpected; higher initial SO_2 concentration results in greater calcium utilization. At 80 ms and 925 °F, calcium utilization for 500 ppmv was 20% compared to nearly 14% measured at 200 ppmv. Higher SO_2 concentration accelerates both kinetic and mass transfer processes. In the shortest residence time examined, the 35 ms case, SO_2 removal increases linearly with the initial SO_2 concentration taken to the 1/2 power. At 35 ms, not much reaction product has formed and, therefore, the mass transfer resistance is low.

Even at the higher CO_2 concentration of 3.4%, calcium carbonate did not form in the spent sorbent. Results suggest that calcium oxide preferentially reacts with SO_2 to form calcium sulfite

rather than forming the carbonate even though there is a difference in concentration of two orders of magnitude.

A pressure-slaked dolomitic hydrate and an atmospherically slaked calcium hydrate were used in this investigation. Both have been used effectively to remove SO_2 from the exhaust of pulverized coal boilers. Past studies on performance of the dolomitic hydrate have shown that it reduces SO_2 more effectively than the calcium hydrate. It was important to determine whether the dolomitic hydrate provides additional SO_2 capture under conditions of low SO_2 concentration found on the coal diesel locomotive.

Figure 5-6 shows data obtained with both sorbents for two SO_2 concentrations, 200 and 500 ppmv. While long-term sulfation results did not produce a difference in removal of SO_2 between the two sorbents, a significant difference in SO_2 capture was measured for residence times less than 100 ms. It is expected that the residence time for diesel exhaust will be between 20 and 80 ms. Twenty ms is the actual residence time if no modification is made to the exhaust duct upstream of the turbocharger. Eighty ms is the maximum residence time that is expected from redesign of the exhaust system. The sulfur removal with dolomitic hydrate was effective in the short term due to its smaller particle size and larger pores, both of which promote rapid penetration of the SO_2 into the interior calcium oxide sites. The results indicate that for short residence times, the dolomitic hydrate captures more sulfur. However, in the case of this dolomitic hydrate, doubling the sorbent mass feed rate is required in order to obtain the same Ca/S atomic ratio as produced from injecting calcium hydrate. It should be noted that, thermodynamically, magnesium oxide in the dolomitic hydrate can be sulfated at these temperatures; however, the reaction rate is thought to be slow. Therefore, there should be little formation of magnesium sulfate at short residence times.

Tests were also carried out to examine how effective calcium sorbents are for NO reduction. The presence of SO_2 and calcium sorbents during low-temperature ($< 400^\circ\text{F}$) capture in duct

scrubbing for boiler applications has been shown to reduce NO emissions. These experiments were performed because data does not exist on NO reduction in the presence of SO₂ and calcium sorbents for coal diesel exhaust conditions, 800 F and 300 ppmv SO₂. An exhaust gas composed of approximately 500 ppmv NO, 3.5% CO₂, and 16% O₂ was produced for these tests. Two SO₂ concentrations, 500 ppmv and 1000 ppmv, were used with the sorbent feed rate selected to produce a Ca/S atomic ratio of 2/1. At the lower initial SO₂ concentration, there was no measured difference in NO levels with or without sorbent present. The initial SO₂ concentration was increased to 1000 ppmv with sorbent feed rate increasing to maintain the Ca/S ratio at 2/1. For this case, a decline of less than 8% in NO was measured. However, the SO₂ levels are two to three times greater than expected in the coal diesel exhaust. While there is uncertainty in the reaction mechanism for the destruction of NO, solid nitrogenous species were detected from analysis of sulfated calcium oxide. This result suggests that at these low temperatures, the NO may operate as an oxidant during the sulfation process in which the NO is reduced to N₂.

Section 6

CONCLUSIONS

Four processes were investigated for the cleanup of gaseous pollutants from coal-diesel exhaust. Two of these processes showed sufficient promise to merit further testing on a larger scale: (1) injection of disposable NaHCO_3 into the exhaust for SO_2 removal only and (2) injection into the exhaust of regenerable $\text{CuO}/\text{Al}_2\text{O}_3$ powder and NH_3 for simultaneous SO_2 and NO_x reduction. The choice between these two processes may ultimately depend on the emissions standards set for the coal diesel exhaust. If NO_x reduction is not deemed necessary, then NaHCO_3 injection appears to be the better alternative. However, if NO_x reduction is required, then $\text{CuO}/\text{Al}_2\text{O}_3$ powder injection should be considered.

For SO_2 removal only, NaHCO_3 performed better than $\text{CuO}/\text{Al}_2\text{O}_3$ powder. The NaHCO_3 demonstrated higher utilization than $\text{CuO}/\text{Al}_2\text{O}_3$ for the same level of SO_2 removal. With sodium bicarbonate, 97% SO_2 reduction was achieved at 49% sorbent utilization; 94% SO_2 reduction was achieved at 63% utilization. For the $\text{CuO}/\text{Al}_2\text{O}_3$ 98% removal was achieved at 39% sorbent utilization. Sodium bicarbonate offers an additional advantage in that 100% of the sorbent particle is reactive. For $\text{CuO}/\text{Al}_2\text{O}_3$ only 10% by weight of the sorbent is reactive; the rest is inert carrier material. Thus, to achieve comparable SO_2 removal, the mass flow of NaHCO_3 required is substantially less than that of $\text{CuO}/\text{Al}_2\text{O}_3$. To reach 95% SO_2 capture, the mass flowrate of $\text{CuO}/\text{Al}_2\text{O}_3$ is six to seven times greater than required for NaHCO_3 . The lower mass flow not only reduces the weight and volume of sorbent carried on the locomotive, but also causes a reduction in pressure drop across the filters. At comparable SO_2 capture, pressure drop was two to three times greater for $\text{CuO}/\text{Al}_2\text{O}_3$ than for NaHCO_3 . This smaller pressure drop, in turn, has positive consequences for engine and turbocharger output.

If NO_x reduction is required, $\text{CuO}/\text{Al}_2\text{O}_3$ is the only option considered that has NO_x reduction capability. Yanmar engine testing showed that with $\text{CuO}/\text{Al}_2\text{O}_3$ powder, up to 97% NO_x removal

can be achieved. Changes in fractional NO_x removal very closely track changes in NH_3/NO_x molar ratio. However, the value of fractional NO_x removal was generally slightly higher than NH_3/NO_x , suggesting that some NH_3 breakthrough was occurring. The only two measurements of NH_3 showed 3% and 6% breakthrough of injected ammonia at NH_3/NO_x values of 0.79 and 0.88, respectively. Because NH_3 itself may be a pollutant, its emissions must be more fully measured in future testing.

GEESI plans to carry out scaled-up testing of NaHCO_3 injection and $\text{CuO}/\text{Al}_2\text{O}_3$ powder injection at GE Transportation Systems in 1992 using exhaust from the single-cylinder coal-diesel engine. These tests will accommodate flows of approximately 500 ACFM, about 10 times the flow from the Yanmar engine tests. The particulate removal system for these tests will consist of envelope filters that were designed and tested at GEESI. In addition GEESI plans to test the fluidized bed system for regeneration of the $\text{CuO}/\text{Al}_2\text{O}_3$ powder and for its separation from coal diesel ash.

The other two options for gas stream cleanup — a CuO pellet granular bed and calcium-based sorbents — were not found suitable for locomotive applications. The CuO pellet granular bed was rejected because a suitable method of particulate removal could not be incorporated into the cleanup system. Although the granular bed performed very well for SO_2 and NO_x , it could not act as the sole particulate cleanup device because of the excessive pressure drop that would be incurred. Because of the bed's large size, additional particulate removal devices could not be added without severely affecting engine performance. Calcium-based sorbents were rejected because of their poor performance under the conditions found in the coal diesel exhaust. For a 300-ppmv SO_2 stream, test results indicated that, at most, only 40% SO_2 capture could be obtained at 20% sorbent utilization.

Section 7
REFERENCES

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Figure 3-1. Bench-Scale Copper Oxide Granular Bed

Figure 3-2. Bench-Scale Granular Bed – SO₂ removal efficiency for 40% CuO sorbent on ZnO/Al₂O₃ substrate

Figure 3-3. Bench-Scale Granular Bed – SO₂ removal efficiency for 32.5% CuO sorbent on SiO₂ substrate

Figure 3-4. Bench-Scale Granular Bed – SO₂ removal efficiency for 5.6% CuO sorbent on gamma alumina substrate: Effect of temperature variation

Figure 3-5. Bench-Scale Granular Bed – SO₂ removal efficiency for 5.6% CuO sorbent on gamma alumina substrate: Effect of velocity variation

Figure 3-6. Bench-Scale Granular Bed – SO₂ removal efficiency for 5.6% CuO sorbent on gamma alumina substrate: Complete saturation

Figure 3-7. Yanmar Engine Copper Oxide Granular Bed

Figure 3-8a. Yanmar Engine Granular Bed – SO₂ removal efficiency for 12% Cu sorbent: SO₂ concentration = 135 ppm and 195 ppm

Figure 3-8b. Yanmar Engine Granular Bed – SO₂ removal efficiency for 12% Cu sorbent: SO₂ concentration = 300 ppm and 895 ppm

Figure 3-8c. Yanmar Engine Granular Bed – SO₂ removal efficiency for 12% Cu sorbent: SO₂ concentration = 1200 ppm

Figure 3-9a. Yanmar Engine Granular Bed – NO_x removal with NH₃ injection:
Start to 680 minutes

Figure 3-9b. Yanmar Engine Granular Bed – NO_x removal with NH₃ injection:
680 minutes to 1300 minutes

Figure 3-10. Bench-Scale CuO Powder Tests – Effect of temperature on SO₂ removal in a 5-mm powder layer

Figure 3-11. Bench-Scale CuO Powder Tests – Effect of velocity on SO₂ removal in 1-mm powder layer

Figure 3-12. Bench-Scale CuO Powder Tests – Effect of velocity on SO₂ removal in 2.5-mm powder layer

Figure 3-13. Bench-Scale CuO Powder Tests – Effect of velocity on SO₂ removal in 5-mm powder layer

Figure 3-14. Yanmar Engine - Candle Filter Test Assembly

Figure 3-15. Yanmar Engine - Candle Filter Layout (top view)

Figure 3-16a. Yanmar Engine Candle Filter Test – Filter pressure drop with CuO Powder (Test 3)

Figure 3-16b. Yanmar Engine Candle Filter Test – SO₂ removal efficiency with CuO Powder (Test 3)

Figure 3-16c. Yanmar Engine Candle Filter Test – NO_x removal efficiency with CuO powder (Test 3)

Figure 3-17a. Yanmar Engine Candle Filter Test – Filter pressure drop with CuO Powder (Test 4)

Figure 3-17b. Yanmar Engine Candle Filter Test – SO_2 removal efficiency with CuO Powder (Test 4)

Figure 3-17c. Yanmar Engine Candle Filter Test – NO_x removal with CuO powder (Test 4)

Figure 3-18a. Yanmar Engine Candle Filter Test – Filter pressure drop with CuO Powder (Test 5)

Figure 3-18b. Yanmar Engine Candle Filter Test – SO₂ removal efficiency with CuO Powder (Test 5)

Figure 3-18c. Yanmar Engine Candle Filter Test – NO_x removal efficiency with CuO powder (Test 5)

Figure 3-19. CuO Powder Regeneration Efficiency

Figure 4-1. Yanmar Engine Candle Filter Test with NaHCO₃ Powder Injection - Candle filter pressure drop

Figure 4-2. Yanmar Engine Candle Filter Test with NaHCO₃ Powder Injection - SO₂ removal efficiency

Figure 5-1. Calcium-Based Sorbent Tests – Schematic of tower reactor

Figure 5-2. Calcium-Based Sorbent Tests – Schematic of sorbent feeding system and venturi

Figure 5-3. Calcium-Based Sorbent Tests – Venturi throat and sorbent injector

Figure 5-4. Calcium-Based Sorbent Tests – Effect of gas temperature on SO₂ capture; Ca/S=2.0; SO₂ concentration = 200 ppm (dry)

Figure 5-5. Calcium -Based Sorbent Tests – Effect of SO₂ concentration on SO₂ capture; Ca/S=2.0; Reactor Temperature=925 °F

Figure 5-6. Calcium-Based Sorbent Tests – SO₂ capture with dolomitic and calcite hydrates; Ca/S=2.0; Reactor Temperature=925 °F

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