

PRODUCTION OF ACTIVATED CHAR FOR CLEANING FLUE GAS FROM INCINERATORS

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ABSTRACT

A granular activated coal char suitable for removing dioxins, furans, mercury, particulate matter, HCl, HF and SO₂ from incinerator flue gas has been produced from the Colchester (Illinois No. 2) coal. Tests with 250 kilogram of this adsorbent on flue gas from a commercial incinerator in Europe demonstrated that its efficiency for removing dioxins and furans was 99.72% to 99.98%. Mercury concentration in the flue gas after the adsorbent was too low to be detected; an efficiency for mercury removal could not be calculated. This adsorbent was produced in three steps from 1 mm by 6.4 mm coal obtained from a commercial Illinois washing plant. The projected cost for manufacturing the adsorbent is lower than that of carbon adsorbents commercially available in the United States (U.S.). The estimated break even cost for the adsorbent from an 80,000 ton/year plant is \$326/ton with a 20% return on investment and a cash flow for 20 years discounted 20% annually.

INTRODUCTION

The U.S. is expected to follow the European lead by imposing low limits for several pollutants from incinerators. The legal emission limits for European waste incinerators were tightened significantly in the late 1980's. Current regulations impose a drastic lowering of the emissions of HCl, HF, SO₂, and mercury on all new incinerators (Table 1) [1]. These regulations apply to existing incinerators in Germany and the Netherlands now, and in Austria by 1996. For the first time emissions of dioxins and furans have been targeted, and are not to exceed 0.1 ng Toxicity Equivalents (TE)/m³ Standard Conditions (SC).

An activated carbon process, developed in the 1970's by STEAG AG of Essen, Germany, to eliminate SO₂ and reduce NO_x emissions, has also shown high removal efficiencies for inorganic and organic compounds such as HCl, heavy metals, dioxins and furans (Table 2) [1]. The first commercial plant using STEAG's activated carbon technology (/a/c/tTM) for cleaning flue gas from a waste incinerator began operation in 1991. Other medical, hazardous and municipal waste incinerators with flue gas outputs of 6,500 m³/h SC to 155,000 m³/h SC have been equipped with this process. Four plants were operating in Europe in 1993 using STEAG's /a/c/tTM-process and three more will be on line cleaning an additional 1.3 MM m³/h by year's end. STEAG has begun licensing its process in the U.S.

Staff members of the Illinois State Geological Survey (ISGS) became aware in 1993 that a U.S. supplier of a carbon adsorbent suitable for STEAG's /a/c/tTM-process was needed [1]. To be acceptable the adsorbent must pass a NO_x self heating test. In this test, the adsorbent is saturated with nitric oxide and the gas flow is discontinued. The temperature rise due to the heat of reaction is measured. It is typically related to the surface area. STEAG's European licensees use adsorbent called German Herdofenkoks that is manufactured from a German brown coal (lignite). This adsorbent has a surface area less than 300 m²/g (N₂ BET). Carbons commercially available in the U.S. have higher surface areas and are reported to fail this test. Not only this safety problem but also the prices for U.S. carbons preclude their use in STEAG's once-through process. The Herdofenkoks adsorbent was reported to sell in Europe for the equivalent of \$300(U.S.)/ton in May 1995.

Mild gasification (MG) of Illinois coals and research on the char that accompanies this process have been active areas of research at the ISGS since the early 1980s [2]. Recent results show that, by selecting appropriate conditions during MG and following MG with a low temperature (< 475°C) oxidation step, a high-sulfur Illinois coal that emits more than 5 lbs SO₂/MMBtu can be converted to char that emits less than 2.5 lbs SO₂/MMBtu [3,4,5]. This partial gasification by low temperature oxidation not only lowers the sulfur content but also activates the chars providing a product that has as much as 300 m²/g N₂ BET surface area [6]. These results encouraged ISGS researchers to believe an adsorbent satisfactory for a STEAG /a/c/tTM type process could be produced from an Illinois coal without the extensive cleaning to remove ash, extensive preoxidation times ("baking") and the briquetting that are a part of costly steps required to make high surface area activated carbon.

EXPERIMENTAL

Coal

Freeman United Coal Company has a size consist of zero by 6.4 mm at one point in its plant that cleans the Colchester seam coal mined near Industry, Illinois. Twelve barrels of this size consist was made available by Freeman United Coal Company for the work described herein. It was spread at about two to four inches depth on the floor to dry overnight before removing the minus 16 mesh (< 1 mm) material by screening. A typical analysis for the Colchester coal appears in Table 4.

Equipment

Pound quantities of activated char were produced in a Model RT-472-104 continuous feed rotary tube kiln (CFRK), manufactured by the Pereny Equipment Company, Inc., of Columbus, Ohio. The CFRK consists of a 10.2 cm ID, 1.83 m long rotating tube of HX alloy. The center portion of the tube (1.4 m) is heated by three separate electrically heated furnaces. The sample is introduced into the tube using a screw type feeder.

A **continuous feed charring oven (CFCO)** was also used in the pyrolysis step because it was better suited to handle large amounts of tar evolved in longer runs. The coal sample was conveyed through a 15.2 cm x 15.2 cm x 69 cm oven on a belt of close-fitting, overlapping, stainless-steel trays (12.7 cm wide) attached to links of a chain drive and heated above and below by tubular electric heating elements. A hopper that controls the bed depth fills the trays as they enter the oven. Evolved gases are removed counter to the direction of the coal and are drawn out an exhaust pipe where volatile materials are burned before being released into the fume hood. All areas outside the heating zone are enclosed in a reasonably tight sheet-metal housing which may be purged with nitrogen to exclude air and avoid loss of char due to burning. Chars were prepared in the CFCO using feed rates of 1-4 pounds per hour, bed depths of 8-20 mm, temperatures of 400-500°C and residence times of 0.25-0.75 h.

A 50 cm I.D. x 1.22 m long (19.5" x 4') (active heated length), stainless steel shell, **batch rotary kiln (BRK)** manufactured by AMS was heated by natural gas burners. It had internal material bed disturbers, bed and gas thermocouples, system thermocouples, and off-gas combustion chamber. Nitrogen or steam purging and a nitrogen cooled sampling probe were available. The maximum operating temperature was 1000°C. A 10% loading required 0.83 cubic feet of coal.

A 20 cm x 0.91 m (8"x36") **continuous feed rotary kiln (CFRK)** was heated by 7 gas burners monitored by three external and two internal thermocouples. The feeder was an AMS fashioned volumetric belt that fed 13.2-15.4 kg (6-7#/h) and the cooler a 35.5 cm x 2.29 m long (14" x 7.5') kiln. The off-gas combustor was the one described for the BRK.

A 48 cm x 3 m (18"x10'), indirect fired, **continuous feed rotary kiln (CFRK)** had a variable rotational speed, adjustable slope and a high velocity pulsating burner system (4 burners in the first two zones, 3 in the last zone). The Inconel 601 shell, No. 10 gage thickness, had six 2.54 cm high anti-slide bars. Auxiliary equipment included a 38 cm x 3.7 m (15"x12') rotary cooler (direct air or indirect water), secondary combustion chamber, and a 24 point continuous data logger. This CFRK could accommodate about 200 kg/h (90#/h) feed rate.

Single-point **BET surface areas** of prepared chars were determined from N₂ (77 K) adsorption data obtained at a relative pressure (P/P_0) of 0.30 with a **Monosorb flow apparatus** (Quantachrome Corporation).

The kinetics of **SO₂ adsorption** on selected chars was determined using a Cahn TG-131 thermogravimetric analyzer (TGA) system. In a typical run, a 30-50 mg char sample was placed in a platinum pan and heated at 20°C/min to 120°C in flowing nitrogen. Once the temperature stabilized, the nitrogen flow was switched to one containing 5% O₂, 10% H₂O and the balance nitrogen. Once the weight stabilized, the SO₂ was added in concentrations representative of a typical flue gas (e.g. 2500 ppmv SO₂). The weight gain versus time was recorded by a computerized data acquisition system.

DISCUSSION OF RESULTS

Colchester coal, a high volatile C bituminous coal with a free swelling index of 3 or more, swells, melts, and agglomerates while being charred if it has not been air oxidized. An oxidation step was necessary (1) to maintain approximately the same particle size in the final product as that existing in the 1 mm by 6.4 mm starting material and (2) to retain sufficient initial pore structure to produce the porosity needed in the final product by partial gasification of the char. Surface area is difficult to develop if coal has passed through a melting stage, but loss of particle strength occurs if too much preoxidation occurs. To achieve the desired result in as short a residence time as practical, as high an air oxidation temperature as possible was selected while allowing a margin of safety in avoiding a loss of control due to burning. Conditions of time and temperature during oxidation were selected that gave a preoxidized coal that could be pyrolyzed at 450 to 500°C to provide char that could be activated at 850°C in CO₂ to increase surface area to 150-250 m²/g (N₂ BET)(Table 3) [7,8]. Observe that decreasing the amount of oxidation either by lowering the temperature or decreasing the time resulted in less surface area. The selection of carbon dioxide for developing added porosity at 850°C was influenced by previous experience [9]. This gas provided a flexibility in temperature control not available with steam.

After demonstrating the three-step preparation (preoxidation, pyrolysis and activation) at the ISGS, Allis Mineral Systems (AMS) was engaged to scale up production in equipment located at its Process Research and Test Center in Oak Creek, Wisconsin [10]. The first successful production level at Oak Creek was preoxidation in a 50 cm diameter batch rotary kiln (BRK) with pyrolysis and activation in a 20 cm CFRK. The largest scale production of adsorbent at Oak Creek involved performing all three steps in succession in the 48 cm diameter CFRK which accommodated a feed rate as high as 90 lbs/h. An attempt to conduct all three steps in the batch kiln was unsuccessful; the tar was not removed at a rate sufficient to avoid agglomeration. The importance of removing volatile components as quickly as possible was reinforced during the transition from the preoxidation step to the pyrolysis step in the 48 cm CFRK. About 90 pounds of preoxidized coal remained in the kiln when the kiln temperature was increased rapidly to the pyrolysis temperature. Some agglomeration occurred which may have approached 7 wt% of the final product.

The Oak Creek kilns had dams at the exit end that maintained a bed occupying 10% of the cross sectional area. The ISGS kiln did not have a dam and the bed occupied considerably less than 10% of the cross sectional area. The thicker bed depth decreased the amount of solids exposed to

reaction gas in the preoxidation and activation steps. This meant that each progression to a larger kiln required more time to achieve equivalent products.

A comparison of properties of the German Herdofenkoks and the ISGS Colchester adsorbent is presented in Table 5. The lower density of the ISGS Colchester adsorbent reflects a lower level of preoxidation than ideal (some swelling). The lower surface area, 110 m²/g, than those obtained in the lab scale of operation, 151-236 m²/g (Table 3) reflect a combination of less preoxidation and less activation in the larger kiln. The SO₂ adsorption profiles shown in Figure 1 confirm that the scale up fell short of reaching the full potential of SO₂ capacity possible with Colchester coal. Additionally, this profile shows a much higher rate of SO₂ adsorption in the first few hours. The initial SO₂ uptake is best correlated with active sites, those responsible for the oxidation of SO₂ to SO₃ [11]. Another factor to be considered in the difference in filling rate is the pore structure. There is reason to believe that the pore structure of the Colchester adsorbent differs significantly from that of the Herdofenkoks adsorbent [11]. It remains to be shown how much of this difference in SO₂ adsorption behavior is due to active sites and how much is related to a special network geometry in which outer macro pores feed into interior micro pores. Of practical importance for use in a STEAG *la/c/t*TM-process, is the lower rate of uptake of nitric oxide (Figure 2) by the ISGS Colchester adsorbent.

The preliminary effort to establish a break even cost was based on the flow diagram shown in Figure 3. While the estimate of \$326/ton (Table 7) for product from an 80,000 ton/year plant is very preliminary, it is encouraging for at least one reason. The flow diagram does not reflect economics in residence time under conditions of better gas/solid contact that are known to accompany the use of modified kilns or other types of equipment. The data (Table 6) in STEAG's pilot scale adsorbent, including passing the NO_x self heating test (not shown), qualify this material for use in STEAG's *la/c/t*TM-process.

CONCLUSIONS

Research has demonstrated that Colchester (Illinois No. 2) coal is a promising feedstock for producing an activated char adsorbent for removing pollutants from incinerator flue gas. Not only are the properties of this adsorbent those desired, its estimated break even cost in a dedicated commercial facility, \$326/ton, could make it highly competitive for use in cleaning incinerator flue gas in the U.S. The ISGS Colchester adsorbent is the first adsorbent to be made in the U.S. from a domestic coal that meets requirements of the STEAG *la/c/t*TM-process.

ACKNOWLEDGEMENT & DISCLAIMER

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Table 1. Emission Limits for European Waste Incinerators [1]

	Germany One day mean values	Netherlands One hour mean values	Austria Half hour mean values
Total Dust (mg/m ³)	10	5	15
HCl (mg/m ³)	10	10	10
HF (mg/m ³)	1	1	0.7
SO ₂ (mg/m ³)	50	40	50
NO _x (mg/m ³)	200 ¹	70	100
Hg (mg/m ³)	0.05	0.05	0.05
Dioxins & Furans (ng TE/m ³)	0.1	0.1	0.1

¹ Federal standards, local standards generally at 100 mg/m³

Table 2. Experience with STEAG's /a/c/t/TM-Process [1]

	Medical Waste Incinerator Germany	Medical Waste Incinerator Netherlands	Hazardous Waste Incinerator Netherlands
Total Dust (mg/m ³)	< 2	1	< 0.5
HCl (mg/m ³)	< 1	< 2.2	< 0.19
HF (mg/m ³)	< 0.05	< 0.05	< 0.05
SO ₂ (mg/m ³)	< 2	< 0.6	< 6
NO _x (mg/m ³)	65	343 ¹	177 ¹
Hg (mg/m ³)	< 0.01	< 0.00031	< 0.002
Dioxins & Furans (ng TE/m ³)	0.003	0.00031	0.002

¹ Not equipped with SCR

Table 3. Lab Scale Adsorbent Preparation at the ISGS

Run #	Preoxidation in the CFRK	Pyrolysis	Activation in the CFRK	Surface Area N ₂ BET (m ² /g)
11	Air, 300°C, 2 h	CFRK, CO ₂ , 450°C, 1 h	CO ₂ , 850°C, 1 h	235
12	Air, 280°C, 0.5 h	CFRK, N ₂ , 410°C, 0.5 h	CO ₂ , 850°C, 1 h	151
13	Air, 330°C, 0.75 h	CFRK, CO ₂ , 475°C, 1 h	CO ₂ , 850°C, 1 h	236
14	Air, 220°C, 0.75 h	CFRK, CO ₂ , 475°C, 1 h	CO ₂ , 850°C, 1 h	179
15	Air, 220°C, 1.5 h	CFKO, N ₂ , 475°C, 0.75 h	CO ₂ , 850°C, 0.75 h	230
16	Air, 220°C, 0.75 h	CFKO, N ₂ , 475°C, 0.75 h	CO ₂ , 850°C, 0.75 h	180

Table 4. Typical Analysis
Colchester Coal

Moisture	14.4%
Vol. Matter	39.9%
Fixed Carbon	53.3%
H-T Ash	6.8%
Carbon	74.3%
Hydrogen	5.3%
Nitrogen	1.4%
Oxygen	8.9%
Total Sulfur	3.3%
Sulfatic	0.1%
Pyritic	2.2%
Organic	1.1%
Btu/lb	13,645
FSI	3.8%

Table 5. Comparison of Properties
(Yield: 48% [277 kg from 581 kg coal])

Property	German Herdfenkoks sorberit	ISGS/AMS Colchester sorberit
Bulk density lbs/ft (kg/m ³)	29.8 (413)	23.8 (378)
PROXIMATE (moisture free)		
Hi-Temp. Ash, wt%	8.68	8.27
Volatile Matter, wt%	7.71	4.74
Fixed Carbon, wt%	83.61	86.98
N ₂ BET Surface Area, m ² /g	277	110

Table 6. Results of Testing ISGS Colchester Adsorbent in STEAG's Test Module

	Before Reactor	After Reactor	Adsorption Efficiency
Total Dioxins & Furans			
Test 1 (ng/m ³)	333.3	0.062	99.98 %
Test 2 (ng/m ³)	337.9	0.052	99.98 %
Test 3 (ng/m ³)	282.3	0.789	99.72 %
Cd + Tl			
Test 1 (mg/m ³)	0.0140	0.0012	91 %
Test 2 (mg/m ³)	0.0062	0.0012	81 %
Test 3 (mg/m ³)	0.0052	0.0004	92 %
Hg			
Test 1 (mg/m ³)	0.0177	below det. limit	
Test 2 (mg/m ³)	0.0384	below det. limit	
Test 3 (mg/m ³)	0.0223	below det. limit	
Sb, As, Pb, Cr, Co, Cu, Mn, N, V, Sn			
Test 1 (mg/m ³)	0.2698	0.0744	72 %
Test 2 (mg/m ³)	0.0805	0.0347	57 %
Test 3 (mg/m ³)	0.0634	0.0185	71 %

Table 7. Estimated Break Even Cost in an 80,000 Ton/Year Plant¹

Land purchase price (\$)	100,000	Cost of coal (\$/y)	7,466,667
Building cost (\$) ²	5,000,000	Cost of Natural Gas (\$/y)	2,626,000
Equipment (\$) ²	16,000,000	Cost of Electricity (\$/y)	526,000
Installation (\$)	8,500,000	Cost of lime (to neutralize SO ₂)	300,000
Carbon production (\$)	80,000	Water (2.45MM gal @ \$1/Mgal)	2,450
Percent yield	45	Labor cost	1,540,000
Coal input (t/yr)	177,778	Maintenance cost (5% of \$21MM) ³	1,050,000
Coal price f.o.b. mine, sized 1 mm by 6.4 mm (\$/t)	34	Real estate taxes (\$)	153,000
Coal transportation cost (\$/t)	8	BREAK EVEN COST (\$/ton)⁴	326

¹ Assume it takes one year to construct the plant, and the plant produces at design capacity thereafter.

² Depreciation (7 Yr st. line) on \$21MM.

³ Operating costs are raised 3% per year.

⁴ Interest on undepreciated value at 20%/yr, net present value at 20% discount rate, 20 years of operation.

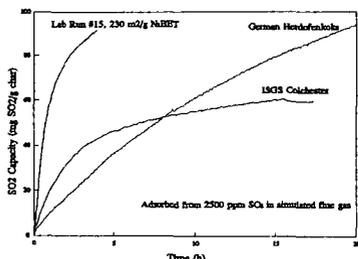


Figure 1. SO₂ Adsorption

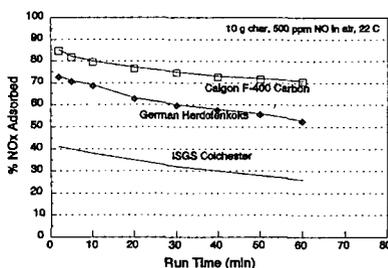


Figure 2. NO_x Removal

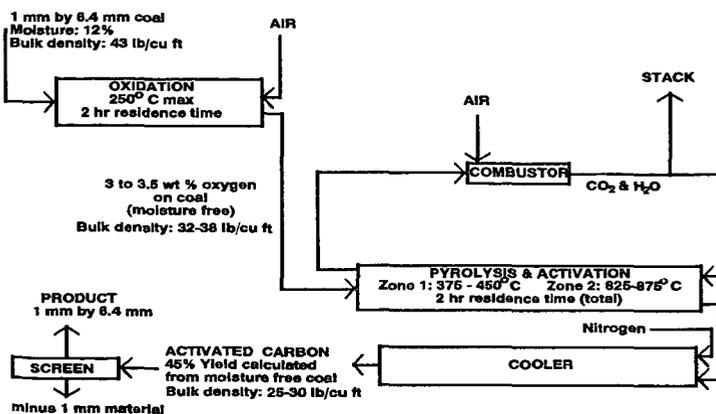


Figure 3. Flow Diagram for a Plant Producing Adsorbent from Colchester (Illinois No. 2) Coal