

ACTIVATED CARBONS FROM NORTH DAKOTA LIGNITE AND LEONARDITE

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INTRODUCTION

The EERC is undertaking a research and development program on carbon development, part of which is directed towards investigating the key parameters in the preparation of activated carbons from low-rank coals indigenous to North Dakota. Carbons have been prepared and characterized for potential sorption applications in flue gas and waste liquid streams.

Lignite, owing to its wide occurrence and variability in properties, has received significant attention as a precursor of active carbon manufacture. Mineral matter content and its alkaline nature are two highly variable properties that can have important consequences on the production of suitable activated carbons. Other factors affecting the production include carbonizing conditions, the activation agents, activation temperature, and activation time (1, 2). However, as previously noted, the relationship between the above factors and the sorption activity is particularly complex (2). Part of the difficulty is that sorption activity encompasses at least three parameters, namely, surface area, pore distribution, and surface acidity/basicity. The presence of mineral matter in the coal can affect not only carbonization but also the activation and subsequent sorption and desorption processes.

Lignite-based activated carbons typically have a low micropore volume, some 17% of the pores being micropores versus 35%–50% macropores (3). The macropores contribute little to the surface area and hence have a small impact on the adsorption process. Samaras, Diamadopoulos, and Sakellariopoulos (4) have recently shown that the removal of mineral matter improves the micropore volume of activated carbons since the mineral matter catalyzes the pyrolysis and carbonization reactions, leading to an enlargement of the pores. Several inorganic species, such as Fe, K, Mg, Ca, and Na are likely gasification catalysts, but the mechanism is not well understood. Removal of mineral matter from lignites decreases the reactivity of the chars towards carbon dioxide and oxygen (5) and produces random changes in the surface area as a result of structural changes (6).

As well as surface area and surface heterogeneity, the presence and structure of particular oxygen surface groups are also important for the adsorption of specific gases or vapors (7, 8). Basic oxygen groups with a pyronic structure, for instance, favor the adsorption of sulfur dioxide (9). Furthermore, Davini (10) has recently demonstrated that carbons containing a significant mineral matter content, particularly if an appreciable amount of iron is present, and an enhanced content of acidic oxygen groups have reduced capacity for SO₂ sorption.

This paper reports recent results of an investigation of demineralization, carbonization temperature, activation temperature, and activation time for one lignite and one leonardite from North Dakota. The majority of the work has been carried out with leonardite. This work is developing further data and understanding on leonardite char adsorbents reported earlier in a patent by Knudson (11).

EXPERIMENTAL

The feedstocks included a Beulah-Zap lignite and a Georesources leonardite. The coals were crushed, ground, and sieved in the usual manner to recover the -10 x 30- or -12 x 30-mesh fraction for testing. The coal analyses (thermogravimetric [TGA] and proximate) are shown in Table 1. The composition of the mineral matter of the leonardite by x-ray fluorescence was also determined.

Two reactors were used to produce the chars, a large capacity (100 grams) TGA unit and a nominally 12-kg capacity Cress kiln (model X31TC). The latter has a bottom distributor plate through which gas, preheated by the kiln, enters to permeate the bed. The chars were activated in the TGA unit or a Lindbergh Type 59344 furnace (TF) incorporating a 19-inch-long by 1-inch-diameter Vycor tube.

A representative sample of the leonardite containing a high mineral matter content was physically and chemically cleaned. Physical cleaning involved float-sink with Certi-grav and using the 1.4 and 1.6 float fractions. Both hydrochloric and hydrofluoric acids were used for chemical cleaning.

The initial carbonization conditions were as follows:

1. TGA unit — Approximately 50 g of feed was carbonized at 700°C to 850°C under N₂ for up to 1 hour followed by steam activation at the same temperature for up to 1 hour.
2. Kiln vessel — Approximately 12 kg of feed was at 480°C under N₂ for 1 hour. Subsequently, the leonardite was carbonized at different temperatures (see below).

Table 2 lists the conditions for activating the leonardite carbonized at 480°C in the kiln. Once the optimum activation temperature was established, the optimum activation time was determined by repeating the test conditions. Table 3 shows the variables used in optimizing the conditions for sorbent preparation from the leonardite. Beulah lignite was activated at 750°C for 20 minutes under 20% steam in nitrogen.

TABLE 1
Coal and Char Proximate Analyses

Coal	Carbonization Temp., °C	Activation Temp., °C	wt%, ar* Moisture	wt%, mf** Volatiles	wt%, mf Fixed C	wt%, mf Ash
Geo*	NA**	NA	32.6	44.1	27.6	28.3
Geo-1.6 Float	NA	NA	22.3	38.4	51.7	9.9
Geo-1.4 Float	NA	NA	42.9	51.2	41.8	7.0
Beulah	NA	NA	31.8	43.9	49.9	6.2
Geo	480	NA	5.3	32.8	47.2	20.0
Geo	480	700	1.1	8.7	52.6	38.6
Geo	480	750	1.1	8.4	53.6	38.0
Geo	480	800	0.9	7.0	57.6	35.5
Beulah	750	750	1.6	6.6	79.7	13.7

* As-received.
 ** Moisture-free.
 * Georesources leonardite.
 ** Not applicable.

TABLE 2
Test Conditions for Activating Georesources Leonardite Char Carbonized at 480°C in the Kiln Reactor*

Test No.	Sample Size, g	Reactor	Temperature, °C
1	10	TGA	700
2	10	TGA	750
3	10	TGA	800
4	10	TGA	850
5	50	TF	800
6	50	TF	850
7	50	TF	900
8	50	TF	950
9	50	TF	1000

* All samples were activated in 20% steam in nitrogen for 10 minutes.

TABLE 3
Test Conditions for Optimizing Char Sorbent Preparation

Variable	Condition
Activation Time under Steam	0, 10, 20, 40, 60 minutes
Coal Cleaning Prior to Charring	1.4, 1.6 Float; HCl, HCl/HF leach
Carbonization Temp.	350, 480, 550°C
Carbonization Temp.	350, 480, 550°C
Activation Temp.	750°C
Activation Gas	Steam, steam/O ₂
Gas-Char Contact Time	10, 20, 20 (steam)/5 (O ₂) minutes

The activating agent was steam in nitrogen, with an approximate concentration range of 20% v/v. In one case, the leonardite char was activated with steam for 20 minutes followed by 3.5% v/v oxygen in nitrogen for an additional 5 minutes.

The activated carbons were characterized by TGA proximate analysis, SO₂ sorption in argon at ambient temperature and at 100°C, iodine number, surface area, and pore volume analysis.

RESULTS AND DISCUSSION

Deminerallization of the leonardite reduced the mineral matter to 6.8 wt% on a moisture-free basis with HCl and to 0.4 wt% moisture-free with HF. The proximate analyses of the raw, cleaned, and carbonized leonardite, as a function of carbonization and activation temperatures, are shown in Table 1 along with proximate analysis data for the carbonized lignite. Overall ash levels remain approximately constant with activation temperature for the uncleaned leonardite carbonized at 480°C and steam activated at temperatures of 700°C and above. As expected, volatile matter decreases with increasing activation temperature.

X-ray fluorescence analysis of the leonardite ash revealed that silicon, aluminum, and calcium are the major components, making up around 72 wt% on an oxygen-free basis, but the total weight of these four elements in the leonardite is 10.6 wt% as a consequence of the significantly high mineral matter

content (28.3 wt%) of the feedstock. The presence of calcium may be detrimental in the activation process for achieving microporosity but could be beneficial for assisting in the capture of SO₂.

A limited set of experiments was carried out on the lignite sample. Sorption tests with SO₂ at 100°C and 5000 ppm resulted in a small uptake, 2.4 wt% (g SO₂/100 g char) with fine carbon and 1.9 wt% with carbon pellets containing a binder, the carbons being produced in the TGA unit. Desorption at 100°C yielded a 0.2 and 0.4 wt% change, respectively, for the different samples, whereas desorption between 100° and 400°C yielded 1.0 and 0.9 wt% respectively.

Differences in sorption activity of products from the TGA and tube furnace reactor were seen in the case of the Georesources leonardite. Here the sorption activity was examined as a function of steam activation temperature for leonardite char carbonized at 480°C. Figures 1 and 2 show the SO₂ sorption data for ambient and 100°C conditions, respectively. The dependence of sorption activity on reactor type is less marked at the higher sorption temperature where the sorption capacity of the tube furnace product approached that of the TGA product. Reactor conditions would seem to affect significantly the resultant sorption activity where mass flow fields are appreciably different. The maximum sorption activity at ambient temperature and 100°C appears to occur for char activated between 750° and 800°C (6.1 and 6.8 wt% SO₂, respectively, at ambient temperature). However, the sorption activity is about one-third lower at 100°C (2.3 and 2.4 wt% SO₂, respectively,) than that at ambient temperature.

Owing to the similarity between the trends in Figures 1 and 2, it is feasible to plot the ratio of the two sorption values at the two sorption temperatures against activation temperature, as illustrated in Figure 3. The observed linear relationship leads to the following expression:

$$\%_{\text{Amb}}\text{SO}_2 = 2.79 \times \%_{100^\circ\text{C}}\text{SO}_2$$

Differences between the sorption activity at the two temperatures can be explained by the weakness of the physisorption bonding (Van der Waals) and the decline in relative strength between the Van der Waal's bond and the increasing vibrational component of the bond energy with increasing thermal energy.

The iodine number provides an alternative measure of sorption activity, the results of which are depicted in Figure 4 for the range of activation temperatures examined. Here it is seen more sharply that the optimum activation temperature for uncleaned leonardite char produced at 480°C is 750° to 800°C, corresponding to the SO₂ sorption results at 100°C (see Figure 2). However, the maximum iodine number of 460 mg I₂/g char (590 mg I₂/g C) is at the lower end of the range of that reported (600 to 1450 mg I₂/g C) for a commercial carbon.

Preliminary investigations on optimizing the carbonization and activation of leonardite (uncleaned) show that the maximum sorption activity as measured by SO₂ (5000 and 10,000 ppm in argon at 100°C) to be as follows: carbonizing temperature: 350°C, activation temperature: 750°C, activation time: 20 minutes. The results are shown in Figure 5. Subsequent activation with 3.5% v/v oxygen in nitrogen for an additional 5 minutes reduced the sorption by approximately 17%. This result is presumably due to a lowering of the microporosity as a result of increased burnoff.

Improvements in sorption activity of leonardite were found through physical cleaning. Carbonizing the 1.4 and 1.6 Certi-grav float-sink fractions (10.9 and 7.8 wt% ash, respectively) at 480°C, activation temperature of 750°C, and activation time of 20 minutes yielded 10.9 and 10.1 wt% SO₂, respectively, at 10,000 ppm SO₂ in argon at ambient temperature. The uncleaned leonardite yielded about 20% less SO₂ sorption (8.4 wt%).

Chemical cleaning of leonardite did not lead to successful sorption of SO₂ since both the HCl and HF severely modified the carbon matrix by removing the bridging divalent ions. The remaining gel-like carbonaceous material after carbonizing and activation yielded sorption data that were comparable to that determined for the carbons derived from the uncleaned leonardite. The behavior of acid-washed leonardite is significantly different from that of acid-washed lignite, as determined from our study of chemically cleaned lignite.

The surface areas, determined by N₂ multipoint BET, for the uncleaned and physically cleaned (1.6 float-sink) leonardite char, both steam-activated at 750°C for 20 minutes, were 81.6 m²/g and 90.0 m²/g, respectively. Although physical cleaning enhances the surface area slightly, nonetheless, gasification of leonardite char appears to affect the development of the surface area significantly.

CONCLUSIONS

Enhanced sorption activity towards SO₂ was obtained with physically cleaned leonardite (< 7 wt% ash) activated carbon. The conditions for its production were as follows: carbonization temperature: 480°C, activation temperature: 750°C, activation time with steam: 20 minutes. The best sorption activity determined was 10.9 wt% SO₂ with 10,000 ppm SO₂ in an argon stream. The surface area of the physically cleaned leonardite was 90.0 m²/g. Optimization of these conditions is expected to enhance the adsorptivity of the char significantly.

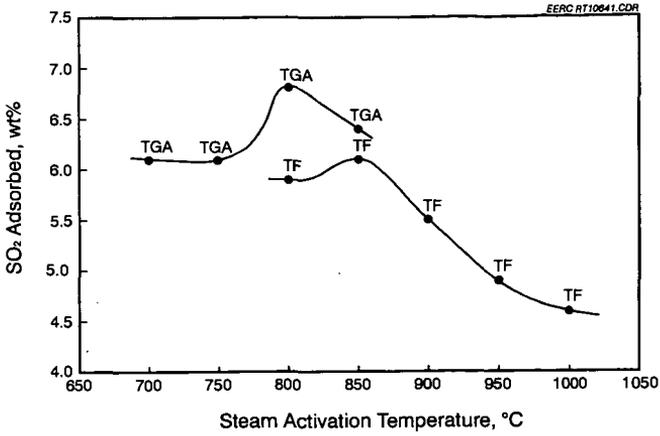


Figure 1. Dependence on activation temperature of SO₂ adsorption from flowing gas containing 5000 ppm SO₂ in argon at ambient temperature for Georesources leonardite (480°C) char.

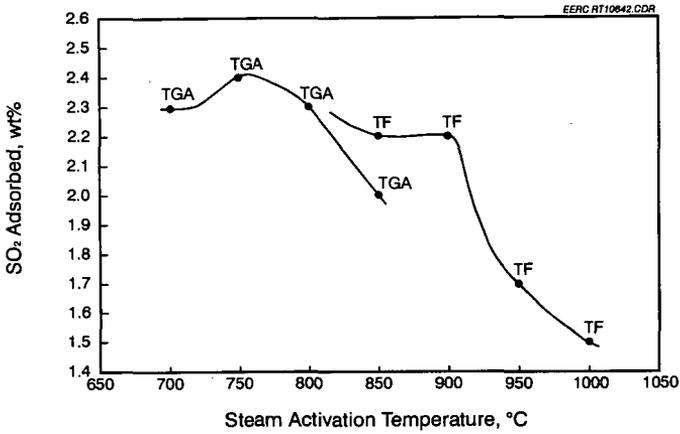


Figure 2. Dependence on activation temperature of leonardite SO₂ adsorption from 5000 ppm SO₂ in argon at 100°C for leonardite (480°C) char.

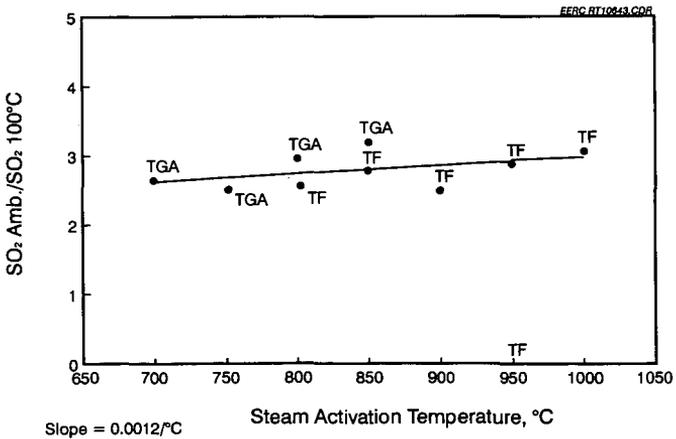


Figure 3. Ratio of SO₂ sorption capacity at ambient temperature to sorption capacity at 100°C for leonardite (480°C) char versus steam activation temperature.

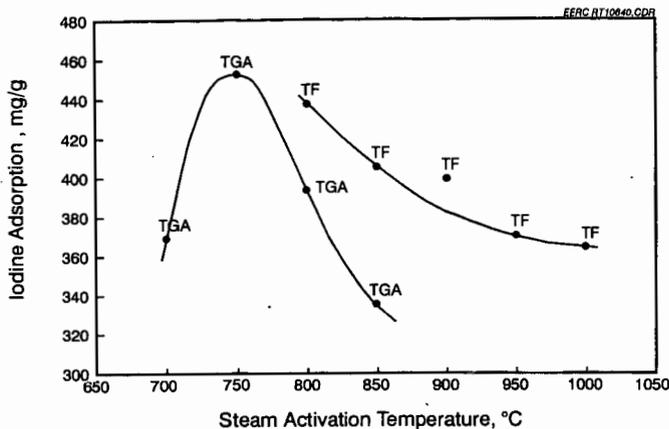


Figure 4. Sorptive capacity for I_2 of uncleaned leonardite (480°C) char steam activated at increasing temperatures.

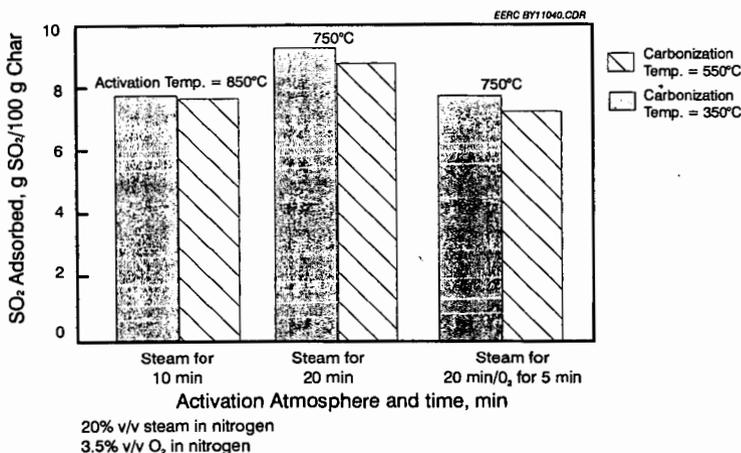


Figure 5. Effect of carbonization temperature and activation gas on SO_2 (10,000 ppm) adsorption at ambient temperature for leonardite chars.

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