

Edwin S. Olson, Brian C. Young,
and Ronald C. Timpe

Energy & Environmental Research Center
University of North Dakota
Grand Forks, ND 58202-9018

INTRODUCTION

Low-rank coals have been extensively investigated for production of activated carbons. Several factors determine the sorption activity of these carbons. The mineral composition and its interaction with the carbonization and activation parameters, including carbonization and activation temperatures, reaction time, and the type of activation reagent gas, seem to be important, but sorption activity and its relation to activation conditions are complex and poorly understood. The sorption activity is governed by several factors including the surface area, pore distribution, surface acidity/basicity, and importantly catalytic functionality.

Carbons prepared from lignites typically exhibit relatively large macropore volumes (1), which contribute little to the surface area and pore volume but render the carbon useful for aqueous sorption where diffusion is slower. In contrast, bituminous coals form carbons with large micropores making them more suitable for gas sorption application. A major factor contributing to the large macroporosity of the lignites is the high concentration of loosely bound inorganic ions that can catalyze gasification and significantly enlarge the pores. This paper discusses the effects of demineralization and carbonization/activation parameters that result in higher and lower sorption characteristics in the low-rank coal carbons.

RESULTS AND DISCUSSION

Leonardite

Chars were prepared by carbonization of GeoResources leonardite at 350, 480, and 550°C. Steam activation of the char was carried out at various temperatures between 700 and 100°C and with several contact times. The maximum surface area was obtained for the carbon activated at 750°C; however, the surface area (N_2 -BET) was only

82 m²/g. Because of the very large amount of alkaline mineral matter (mainly Ca) present in the char, pore enlargement due to gasification of substantial amounts of carbon occurred. Both chemically (HCl) and physically cleaned (float-sink) leonardite were also carbonized and steam-activated. Acid-washing of the leonardite completely changed the coal structure to a gel form, but subsequent charring and activation gave carbons similar to the uncleaned leonardite. The surface area of the 750°C carbon prepared from physically cleaned leonardite was also very low (90.0 m²/g). Thus, calcium-catalyzed pore enlargement is probably still important during activation of this material.

Sorption tests with SO₂ were conducted at two temperatures—ambient and 100°C—on the sets of activated carbons prepared from the chars carbonized at 350, 480, and 550°C. Activation of the 350°C char at 750°C gave the highest sorption capacity (9.2 wt%) at ambient conditions. Under similar activation conditions (750°C) and ambient test conditions, the 480°C char gave a carbon with an adsorption capacity of 8.4 wt%, and the 550°C char gave a carbon with a capacity of 8.7 wt%. Thus, higher and lower activation temperatures gave lower- capacity carbons, but this behavior is not currently understood.

The effect of activation time was also investigated. For the 350°C char, activation for 20 min at 750°C gave the maximum sorption, whereas the 480°C char exhibited a decreasing capacity from time zero. Since the surface areas are very low, most of the sorption must be occurring at the calcium sites. The carbons from chemically cleaned leonardite were low strength and gave variable SO₂ sorption capacities. The physically cleaned leonardite gave a carbon with increased sorption capacity (10.9 wt%). The float-sink cleaning does not remove calcium, but does remove the silica and clay, so activity increased on a sorbent weight basis.

Gascoyne lignite

Gascoyne lignite chars were prepared at 400°C and subsequently steam-activated at 750°C for 30 min. The iodine number of the char was found to be 283, and that of the activated carbon was 290. As with the leonardite chars, the lack of improvement in surface area during steam activation can be attributed to mineral-catalyzed gasification (2). Thus, several experiments with chemically cleaned lignite were performed. Nitric acid-washed Gascoyne was prepared and carbonized at 400°C. The I₂ value was quite low (183), probably because the pores collapsed to a greater extent during carbonization in the absence of the calcium ions. Steam activation (30 min) of the char from the cleaned coal gave an improvement in the I₂ value (238), but this value is still low. Activation of the char prepared from the nitric acid-washed coal at 750°C for 90 min gave a carbon with an iodine number of 422. The char produced from lignite cleaned with sulfurous acid had an I₂ number of 271. Steam activation of this char gave a carbon with I₂ number of 317. Although these values are low compared to those of commercial carbons, they indicate that acid-washing is essential for obtaining usable carbons from low-rank coals. A further demonstration of the mineral effect was obtained by acid-washing the 400°C char prepared from uncleaned coal and then activating the cleaned char. In this case, the I₂ number decreased for the 30-min activation, but increased substantially for the 60-min activation to 454. Thus, the kinetics of steam gasification in the absence of the calcium are very slow, and a long activation time is required to develop the desired porosity. Experiments to obtain sorption data for SO₂ and mercury are in progress.

Beluga subbituminous coal

Very low surface areas were obtained by steam activation of the chars produced from the very low-ash Beluga subbituminous coal. Since the surface areas were small, the capacities were not large. However, mercury sorption rates were determined for several of the carbons and chars in the air flow at 150°C, using a continuous mercury vapor UV detector. The initial char removed 10% of the mercury, compared to an 86% removal rate for the activated carbon. For a sulfur-treated Beluga char, the removal rate was 32%, whereas after activation of the sulfur-treated char, the removal rate was 57%. No activity was observed in nitrogen

at 150°C, since the sorption process at this temperature is entirely oxidative chemisorption. These data suggest that the sulfur is not important to obtaining high Hg removal rates, although the sulfur may affect the capacity of the carbon.

CONCLUSIONS

Surface areas for low-rank coal chars and carbons were low but improved substantially by acid-washing. Sorption capacities and rates were determined by other factors, such as calcium and sulfur contents of the carbons.

REFERENCES

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