

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report
of
Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Melville Richard Lee for the degree of Chemical Engineer. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Chemical Engineer.

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An Attempt to Make Low-Sulphur Coke
from High-Sulphur Coal.

A Thesis
Submitted to the Graduate Faculty
of the
University of Minnesota
by
Melville R. Lee.

In partial fulfillment of the requirements
for the
degree of
Chemical Engineer.

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OBJECT. Altho much of the coal from the Illinois fields has excellent coking properties it will have no value as a raw material for metallurgical coke until some method has been devised for removing the sulphur during, or following, the coking period. This thesis has been an attempt to develop such a process.

HISTORICAL. There are two methods of reducing the sulphur in coke which have been tried up to the present time.

The first of these processes is the "wash" *(a) process. Coal after being crushed, previous to coking, is put thru a separation process which involves the use of a salt solution of specified specific gravity. The sulphur is in the finest material, for the most part, and this fine material is separated by "jigging" the coal in the liquid. The "fines" are floated off in suspension.

The second method is that proposed by Parr and Powell*(b). Their method consists of passing inert gas such as hydrogen, nitrogen, or sulphur-free coal gas thru the coal during the coking period.

* The letter refers to the bibliography.

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In order to check this last method ten grams of coal was coked in a gas muffle, the gasses being allowed to come out one end the other end stopped. Next, ten grams of the same coal was coked under the same condition except that hydrogen chloride gas was passed over the coal during coking. An analysis of the coke produced showed that while the plain coke contained ninety-eight hundredths of one per cent sulphur. The coke treated with the gas showed only fifty-eight hundredths of one per cent sulphur.

Analyses of sulphur were made by the Eschka method in this case and in all those following.

THEORY OF METHOD. Sulphur in coal is present in the form of pyrites, sulphates, free sulphur, and organic compounds. By mixing slaked lime intimately with the coal previously to coking an attempt to fix the sulphur present in the form of calcium sulphide was made. Slaked lime was used in preference to the oxide due to the fact that the reaction between lime and organic sulphides is supposed to be facilitated by moisture, (c) also because the moisture would be changed to hydrogen gas and carbon monoxide. The presence of hydrogen facilitates sulphur removal according to the work done in the Illinois State Laboratories, after coking, the product was: 1. Treated with hydrochloric acid to decompose the calcium

salt to give up the sulphur in the form of hydrogen sulfide according to the following reaction $\text{CaS} + 2\text{HCl}$ equals CaCl_2 plus H_2S . 2. Treated with steam under pressure to hydrolyze the salt and break it down as far as possible according to the equation $\text{CaS} + 2\text{H}_2\text{O}$ equals $\text{Ca}(\text{OH})_2$ plus H_2S . This stage probably cannot be reached, a part of the salt will form a basic sulfide. Care must be exercised to exclude air when treating the coke with acid or steam because air will decompose the hydrogen sulfide at the temperature of boiling water and leave an adherent coating of sulphur on the surface of the coke.

DETERMINING THE SIZE OF COAL FOR COKING: In order to insure intimate admixture of the lime throughout the coke mass it is desirable to get the coal into as fine a state of division as is compatible with good coking practice. The first experiments carried on were for the purpose of determining the size of the coal best suited for coking, and the effect, if any, of slaked and unslaked lime on the coking characteristics of the coal. For this part of the work a Franklin county (Illinois) coal was used. Under ordinary conditions a coke of fair quality could be made from this coal. For coking purposes a retort, cup shaped, with a half inch pipe for take-

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off, holding about a pound and a half of coal was used. It was placed in a brick and asbestos shell, heat being supplied by four large burners which were capable of maintaining the bottom half of the retort at a cherry red heat. The coking operation was carried on in each case until combustible gases ceased to come off.

EXPERIMENTAL: Run No. 1. A charge of coal was ground in a ball mill until all of it passed thru a sixty mesh screen. The charge was coked for six hours. The coke formed was an incoherent mass which crumbled when touched.

Run No. 2. A charge of the sixty mesh coal was coked as above but mixed with five per cent calcium oxide. The product was very similar to that of Run No. 1.

Run No. 3. A charge consisting of sixty mesh coal and five per cent slaked lime was coked, but there was no improvement in the coke quality.

Run No. 4. It was decided that the ball mill might reduce a large portion of the coal much below sixty mesh so the coal was passed thru a sample mill until the largest pieces were sixty mesh, but the coke made was little if any better than that made in previous runs.

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Run No. 5. For the next run a coal was used which had been run thru rolls set for twenty mesh. The coke was of good quality - it had fair tensile strength, a metallic ring when struck, and a silver grey color.

Run No. 6. For this run the coal was crushed as in Run No. 5. mixed intimately with five percent slaked lime and coked as before. The product was identical with that of Run No. 5. except that it had a slightly lighter color. The tensile strength of the two cokes was almost the same.

An analysis was run of the coke produced in Run No. 5., an analysis of the original coal and analyses of the coke produced in Run No. 6. after treatment in the following ways: First the coke in pieces as large as walnuts was boiled in a solution of hydrochloric acid, the proportion of acid to water being one to three. Action between the acid and the lime was noticed immediately upon immersing the coke in the solution. Particles of the coke slaked off apparently due to the reaction of the acid and the excess lime in the coke. Boiling was continued until the odor of hydrogen sulfide was no longer noticeable which took nearly two hours. Second, A second sample of the same coke was treated in the following manner: a chamber made from a section

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of six inch pipe, with suitable plugs allowing an entrance at the top for steam and an opening at the bottom which was controlled by a valve opened only enough to insure drainage of condensed steam; baffle plates were placed in the chamber above and below the space left for the coke in such a manner that the coke would not be exposed to a jet of steam as the steam entered or left the chamber. This precaution was taken in order, as nearly as possible, to approximate conditions were the process on a commercial scale. The chamber was charged with coke and steam at a pressure of forty pounds per square inch passed into the chamber and this pressure maintained for a period of one hour. The sizes of the pieces of coke were about the same as those boiled in the acid. The two samples of coke were then allowed to stand exposed to the air for four days in order to dry. The sample boiled in acid was found to have lost a great deal of its strength and crumbled to some extent. On grinding this sample for analysis the inside of the lumps was found to be damp and a strong smell of hydrochloric acid and hydrogen sulfide was noticed. The sample treated with steam was to outward appearances identical with the coke untreated with steam. It was dry inside and had the same strength

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as before treatment.

Below are given the results of the analyses of each coke:

S in coal	S in plain coke	Coke heated with lime and acid	Coke treated with lime and steam
.981%	1.40%	.617%	.745%

The literature contained a statement to the effect that washing plain coke with acid would materially reduce the sulfur content. In order to check this statement a sample of the same coal was coked without mixing lime. Samples of this coke were treated identically as those of the limed coke and the following analyses made, viz:

Plain coke	Plain coke boiled with acid	Plain coke treated with steam
1.4%	.832% S	.585% S

These results would indicate that the best method for treatment was the treatment of plain coke with steam. Due to the fact that Franklin County coal was not primarily a coking coal and that at this time we has received samples of coal which more nearly fulfilled our requirements no more work was done on this sample.

The next coal used was Black Brior Coal, from Williamson County Coal Company of Harrisburg, Illinois. For coking purposes it was run thru twenty mesh rolls. It took about four and one half hours to drive off the

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volatile constituents. The coke was of excellent quality, possessing high tensile strength, silver color, and a metallic ring when struck. The run was made as before with an analysis made of the limed coke as well as of the plain coke. Twenty pounds pressure was used for the steam treatment. The limed coke on being treated with acid crumbled to a lesser extent than in the first series of runs.

The results of analyses of this run are as follows:

Coal.	Plain coke	Limed coke	Plain coke acid treated	Plain coke steam treated
.814	1.08%	1.734	1.023	1.027
Limed coke acid treated		Limed coke Steam treated		
.958		.916		

A very significant fact is shown here. The lime in the coke prevents some of the sulphur from leaving the mass which in the absence of lime is given off in the gases. The lime used in each case was chemically pure so that no error from this source was possible. This method of sulphur was not successful with this coal, due as indicated by the differences observed in the sulphur content of the coals and sulphur content of the plain cokes to some property of the coal itself, probably to the original form of the sulphur in the coal.

The following work was done on Saline County, Illinois, coal obtained from the O'Gara Coal Company, Johnson City, Illinois. The coke produced as in the previous run was equally as good as that made from "Black Briar" coal.

Steam treatment at a pressure of ninety-five pounds was utilized to check roughly any differences which might be traced to differences of steam pressure.

In this instance the coking period was almost four hours.

Results of sulphur determinations:

Coal	Plain Coke	Limed Coke	Plain coke Acid treated	Plain coke Steam treated
.97	1.308	1.668	1.065	1.062
Limed coke acid treated		Limed coke Steam treated		
11.127		1.159		

Due to the fact that limestone is used in the blast furnace, additional amounts of lime in the coal would not be injurious to the coke. A run was made using the same coal as before using ten percent lime instead of five per cent lime. The results were almost identical with those obtained using per cent lime:

Coal	Plain coke	limed coke	limed coke acid treated	limed coke steam treated
.97	1.308	1.67	1.12	1.10

It will be observed that slightly less sulphur

remained in the coke in this case than with five per cent lime.

It would seem from these tests that the lime had reached its maximum efficacy at five per cent. In order to determine just how much sulphur could possibly be removed from this coke the following test was made. Using the above coal the procedure was repeated as before omitting the steam treatment, grinding the coke to a fine dust before treatment with acid. The results of the analyses are as follows:

Coal	Plain coke	Limed coke	Limed coke acid treated	Plain coke acid treated
.978	1.308S	1.668S	.54%S	.68%S

This test proved that the penetration of the acid solution and steam were very imperfect.

Still another test was run to determine whether or not lime would free sulphur from the coke after coking. This was done as follows: Plain coke was ground and mixed with ten per cent lime and heated in a closed retort for two hours. Results are as follows:

Plain coke	Lime treated coke
1.3	1.25

Calculations were on a basis of equal weights of coke.

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The suggestion made by Powell that sulphur was present in the form of a carbon compound in coke was questioned. It being deemed improbable that an organic compound would decompose in acid or steam as we found the sulphur bearing material in the coke to do. In order to check this a determination of the iron in the coke was made. (It being presumed that the S was in the form of sulfide) Next a sample of the coke was pulverized and treated with hydrochloric acid and the enclosed gases passed thru ammoniacal cadmium chloride to precipitate any sulphur, and proceeding with the analysis as is done in the evolution method of sulphur determination in steel.

Results were as follows:

.78% S evolved .965% Fe.

It may be seen that the iron present is not sufficient to unite with all the sulphur as ferrous sulfide, even if all the iron were in the form of a sulfide. The molecular proportions would be, sulphur 32, iron 56 in that case. However, part of the sulfide may be present in the form of other sulfides as well as ferrous sulfide. For example, calcium sulfide.

CONCLUSIONS:- In order that this system be successful, a better method of acid or steam penetration would need to be devised in order to remove the sulphur.

Steam treatment is preferential, producing at once a dryer coke, more economically.

On the other hand, treatment with lime may fix the sulphur in the form of calcium sulfide. It is a well known metallurgical fact that calcium sulfide is dissolved by basic slag. If we have the sulphur in this form then in the place of in the form of a carbon compound the sulphur content of the metal produced would probably be reduced.

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