REMOVAL OF SODIUM FROM LIGNITE BY ION EXCHANGING WITH CALCIUM CHLORIDE SOLUTIONS

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Lignite resources in North Dakota are estimated at 350 billion tons, comprising 20 percent of the nation's total coal resources on a tonnage basis. Using present technology, 16 billion tons of this lignite is mineable (1). Analyses of over 400 samples of coal taken throughout the region show that the average sodium oxide content is 5.5 percent of the ash (2).

The major use of lignite is as fuel for electric power generation. These large power plants (up to 450 MW) cannot operate efficiently burning high sodium lignite because of fouling of heat transfer surfaces. Field tests and boiler experience have shown that when sodium oxide content in the ash becomes greater than 5 percent, excessive boiler fouling can be expected (3).

Sodium does not occur as in the discrete mineral particles in lignite but is evenly dispersed throughout the coal matrix (4,5). Sodium, along with calcium, magnesium, iron and aluminum cation, is attached to exchange sites on the lignite structure and can be replaced by ion exchange with other elements (6). Combustion tests using lignite in which sodium has been replaced by calcium in ion exchange have shown less fouling than untreated lignite.

This paper presents selected results based on laboratory batch tests in which calcium from calcium chloride solution is used to replace sodium in a high sodium lignite. Test parameters include coal moisture content, particle size, solution concentration, temperature, solid-to-liquid ratio and contact time.

EXPERIMENTAL PROCEDURE

Lignite selected for the tests was from the Beulah mine (North Dakota) and contained 8.7 percent sodium oxide in the ash. Ash analysis, as determined by x-ray fluorescence, is shown in Table 1. Ash content of the coal was 10.8 percent on a dry basis.

Table 1. - Ash Analysis of Test Coal by X-ray Fluorescents: (Beulah mine, North Dakota)

Element	Percent
SiO	19.7
Al_2O_3	12.0
Fe_2O_3	7.6
TiO_2	0.5
P_2O_5	0.3

CaO	19.3
MgO	5.2
Na_2O	8.7
K_2O	0.7
SO_3	25.0
TOTAL	99.0

The test coal was crushed to desired size and stored in double plastic bags to minimize moisture loss. The test procedure consisted of combining the desired weight ratio of lignite with calcium chloride solution in a 400 ml beaker and stirring with a propeller-type mixer for the specified length of time. The lignite was separated from solution by filtering with a Buchner funnel using Whatman No. 41 filter paper. The filtrate was analyzed for pH and specific gravity, and the dissolved elements were measured by an inductively coupled argon plasma spectrometer (ICAP). The lignite was rinsed with 200 ml deionized water and filtered. This filtrate was also analyzed. The coal sample was dried and ashed, and the ash analyzed by x-ray fluorescence spectrometry.

RESULTS AND DISCUSSION

Each of the test parameters is discussed individually.

Coal Moisture

The relationship between the extent of sodium removal by ion exchange and lignite moisture content is shown in Figure 1. Moisture reduction was accomplished by air drying the lignite at 25°C. In this set of tests, coal sized to 80 x 0 mesh was contacted with .05 molar calcium chloride solution for 5 minutes. The coal-to-liquid weight ratio was 1 to 4. The moisture content of the coal varied from 34 to 15 percent. Results indicate that reducing the coal moisture to 28 percent had little effect on the rate of exchange. Below 28 percent moisture, the rate of exchange was reduced considerably.

Lignite has a porous structure and the inherent water is believed to be trapped in capillaries (7). Organically bound ions such as sodium may adhere to the surface of the capillaries. In the ion exchange process, calcium diffuses from the solution into the water-filled passages and replaces sodium. Reducing the lignite's moisture content collapses and seals off a portion of the capillary thus reducing ion exchange potential.

Particle Size

The effect of particle size on the rate of ion exchange is shown in Figure 2. In this set of tests, various sized coal was treated with .05 molar $CaCl_2$ for 5 minutes at solid to liquid weight ratio of 1 to 4. Coal moisture content was 34 percent.

Results show that treating 40 x 0 mesh lignite reduced the sodium content in the lignite by 80 percent, while treating 8 x 0 mesh, at the same test conditions, reduced the sodium by 63 percent. Treating ¼ x 0 inch sized lignite removed only 15 percent of the sodium originally in the coal. The lignite's particle size determines the distance that the exchanging ion must travel through the capillary network and, for that reason, effects the rate and extent of exchange.

Solution Concentration

The sodium content of the treated lignite (dry basis) as a function of starting calcium concentration in solution is shown in Figure 3. The calcium content of lignite resulting from the treatment is also shown. In this series of tests, calcium chloride solution in molar concentration varying from 0 to .2 molarity was mixed with 80 x 0 mesh lignite for 3 minutes. The solid-to-liquid weight ratio was 1 to 5.

Results indicate a direct relationship between solution concentration and sodium removal. The calcium content of the lignite increases proportionally to the decrease in sodium content.

Temperature

The relationship between the temperature of the calcium solution and sodium removal is shown in Figure 4. In this test series, 8 x 0 mesh lignite was treated with .05 molar $CaCl_2$ solution for 5 minutes. The solid-to-liquid ratio was 1 to 4. The solution temperature was varied from 70 to 145 degrees F. Results indicate that 63 percent of the sodium was removed from the lignite at 70 degrees F., while 72 percent was removed at 120 degrees F. Temperatures higher than 120 degrees F. did not increase the removal efficiency.

Figure 5 shows the moles of sodium removed from the lignite per mole of calcium added as a function of temperature. Under these test conditions, one mole of calcium will replace 1.15 to 1.25 moles of sodium. Under ideal conditions, this ratio should be two sodiums removed for every calcium added. In the present case, other metals in the lignite, such as magnesium or iron, which are also ion exchangeable, may have been replaced, thus reducing the molar ratio of calcium replacing sodium.

Solid-Liquid Weight Ratio

The solid-to-liquid ratio effects sodium removal efficiency as is shown in Figure 6. In this series of tests, lignite sized 8 x 0 mesh was contacted with .05 molar calcium chloride for 5 minutes. The solid-to-liquid weight ratios were 1 to 2, 3 to 8, and 1 to 4.

Results in Figure 6 show that increasing the quantity of liquid (thus increasing the quantity of calcium present) in proportion to solids will increase the sodium removed. The reason is that with higher ratios more calcium is in contact with the coal. Figure 7 shows the ratio of moles of sodium removed to moles of calcium added to the lignite for this set of tests. As shown, the molar quantity of sodium removed to calcium added to the coal varied from 1.25 to 1.35 and compared favorably to that previously shown in Figure 5.

Contact Time

The effect of solid-liquid contact time on sodium removal efficiency is shown in Figure 8. In this series of tests, .05 molar $CaCl_2$ solution was mixed with 8 x 0 mesh lignite in a weighed solid-to-liquid ratio of 1 to 4. Contact time was 5, 30 and 120 minutes.

Results show that the quantity of sodium removed for this size coal increased with contact time up to 30 minutes. After 30 minutes, there was no significant increase. This indicates that equilibrium under these test conditions with this size limit has been achieved in less than 30 minutes.

SUMMARY

The quantity of sodium removed from lignite by ion exchange with calcium is a function of the coal's moisture content, particle size, quantity of calcium present in solution, solution temperature and contact time. The greatest exchange occured with lignite containing more than 28 percent moisture and smallest particle size (80 mesh x 0). The rate of exchange increases slightly with temperature to 120°F. The sodium removal is a direct function of solution calcium concentration. Solution concentration and solid-liquid ratio are interdependent variables which determine total quantity of calcium which contacts a unit quantity of lignite.

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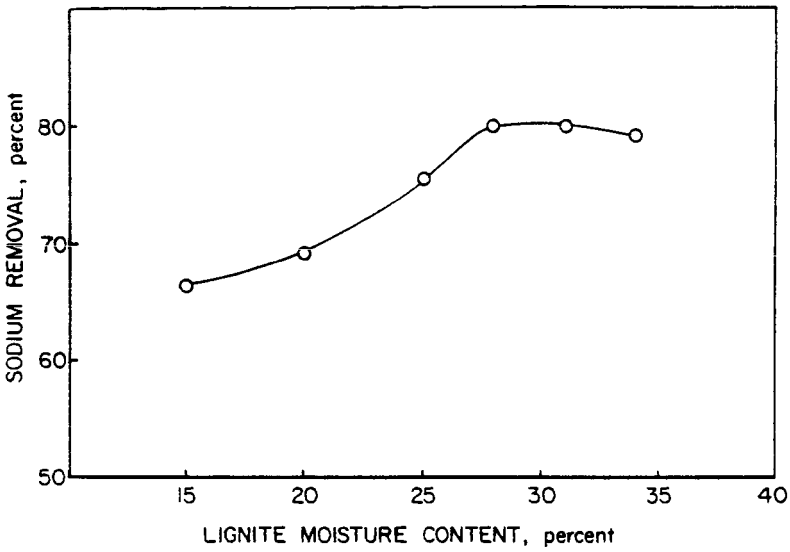

FIGURE 1. - Sodium removal as a function of lignite moisture content.

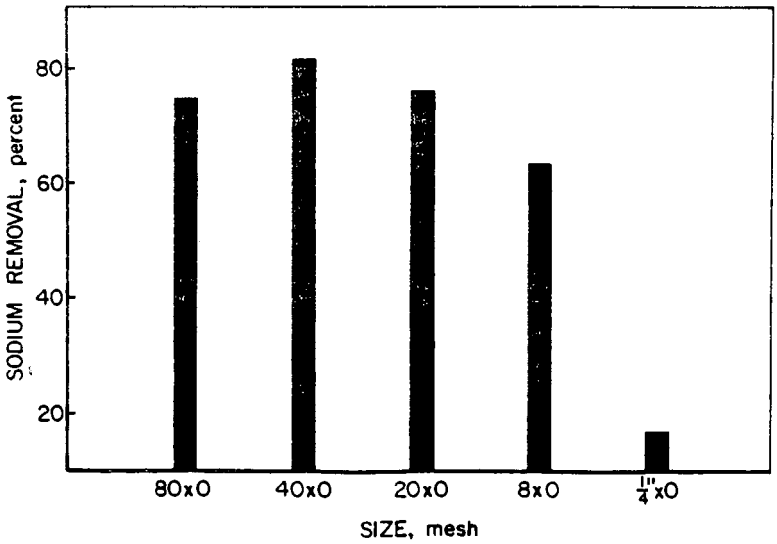

FIGURE 2. - Sodium removal as a function of lignite particle size.

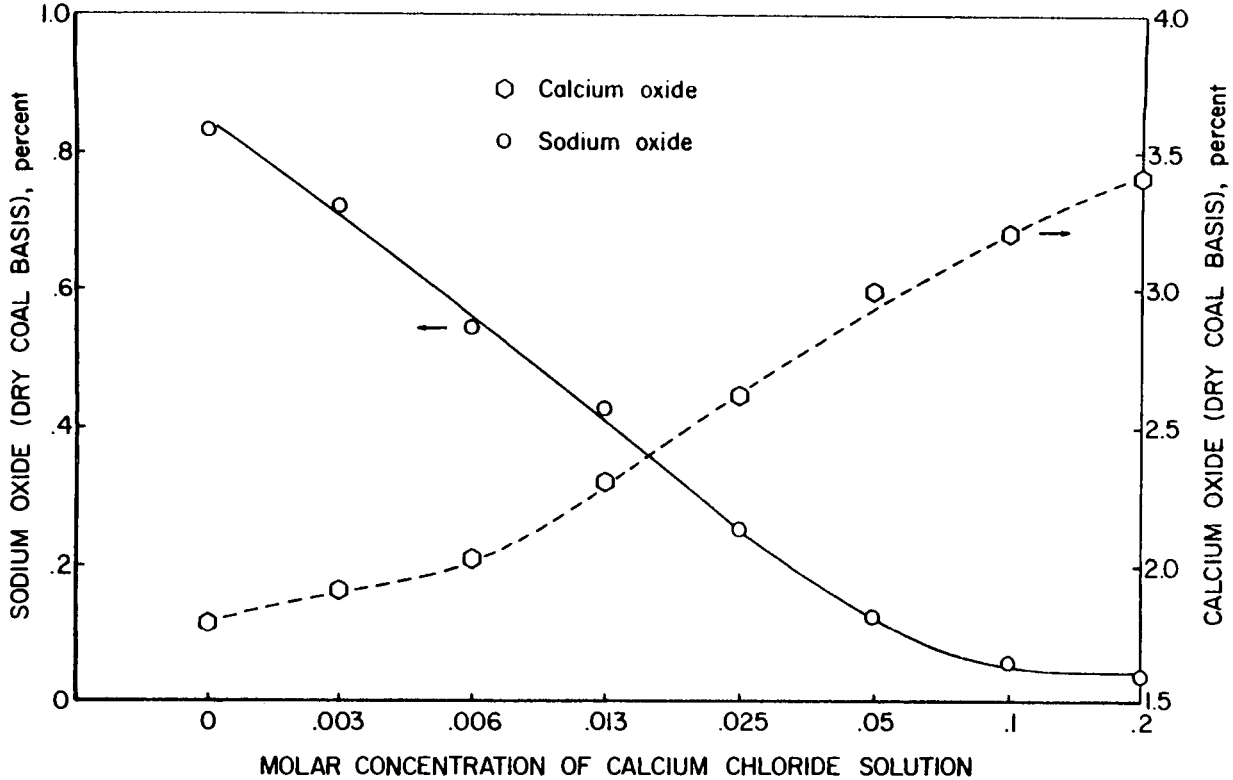

FIGURE 3. - Sodium removal and calcium addition to lignite as a function of calcium chloride solution concentration.

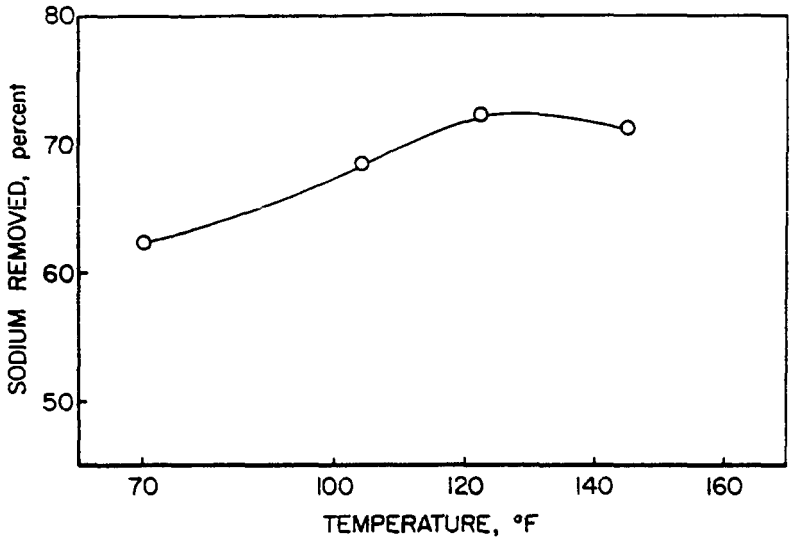

FIGURE 4. - Sodium removal from lignite as a function of temperature of treating solution.

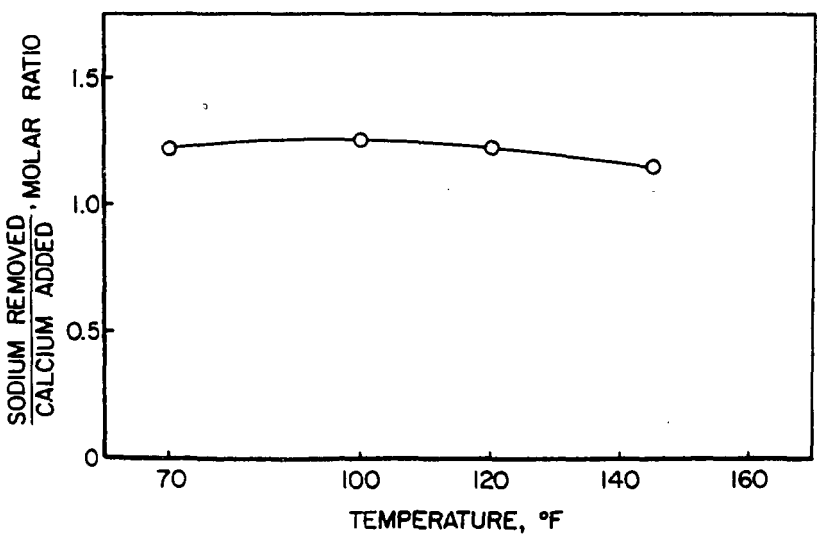

FIGURE 5. - Ratio of sodium removal from lignite to calcium added as a function of solution temperature.

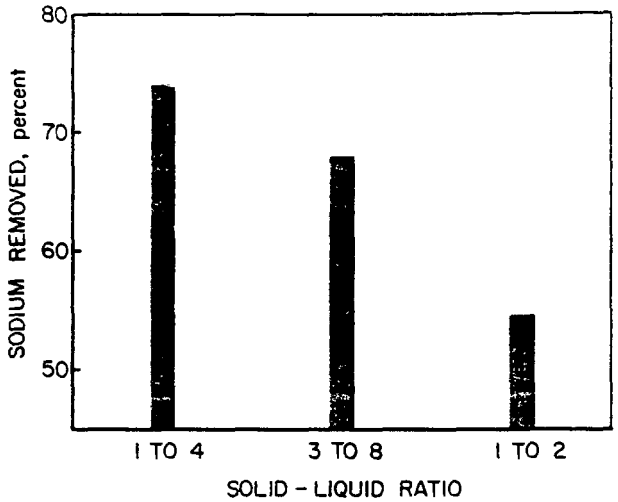

FIGURE 6. - Sodium removal from lignite as a function of solid to liquid ratio.

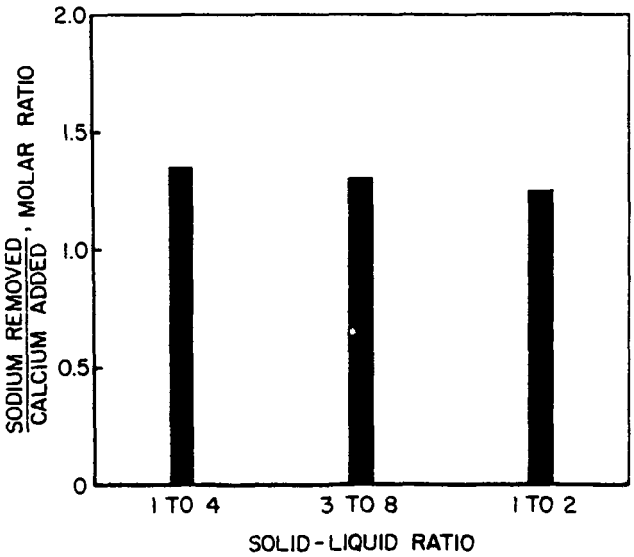

FIGURE 7. - Ratio of sodium removal from the lignite to calcium added as a function of solid to liquid ratio.

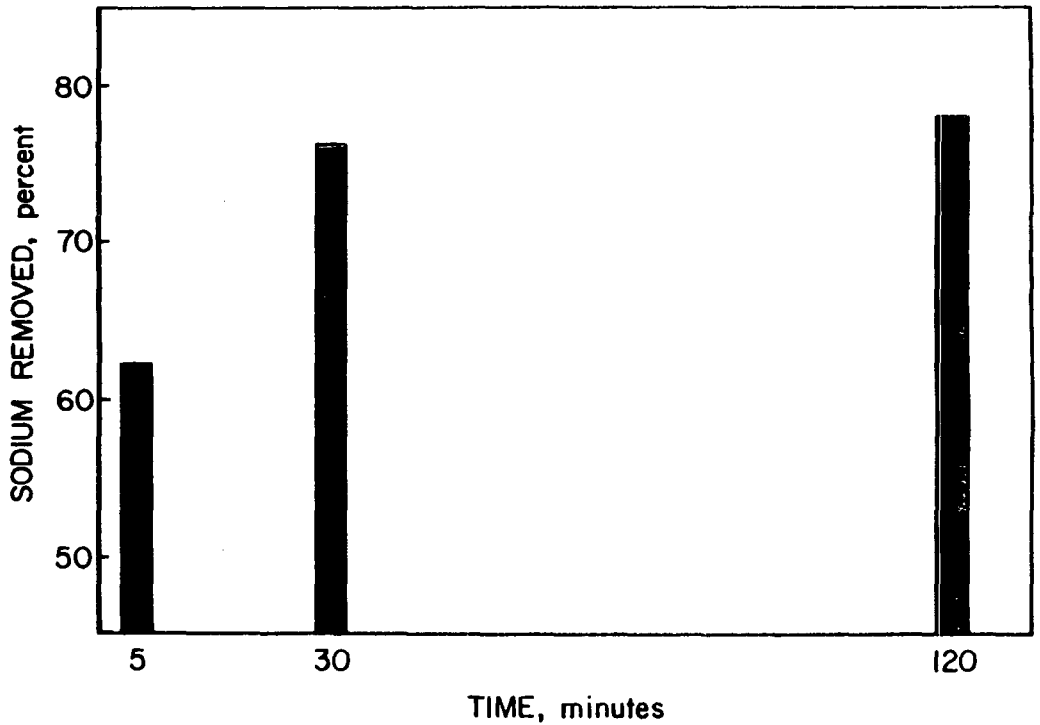

FIGURE 8. - Sodium removal from lignite as a function of solid-liquid contact time.