

Behavior of Quartz, Kaolinite, and Pyrite during Alkaline Leaching of Coal

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Most of the mineral matter was extracted from Illinois No. 6 coal, a representative bituminous coal, by first leaching it with a hot alkaline solution and then with a dilute mineral acid. The alkalis employed, in decreasing effectiveness, were: (1) NaOH, (2) Na₂CO₃, (3) NaHCO₃. The results generally agreed with those obtained in leaching quartz, kaolinite, and iron pyrite individually under similar conditions. The quartz was solubilized by the stronger alkalis. Kaolinite was largely converted to sodium hydroaluminosilicates such as analcime, hydroxycancrinite, and natrodavynite. A portion of the iron pyrite was converted to hematite, the amount depending on alkali strength and temperature. The sodium hydroaluminosilicates and hematite were subsequently extracted by acid.

Previous work has shown that ash-forming mineral matter, including iron pyrites, can be removed from coal by leaching the finely divided material with a hot caustic solution under pressure followed by washing with a dilute mineral acid (1-6). Recently, similar results have been achieved in leaching fine-size coal with hot sodium carbonate solutions (7). In both cases, quartz appears to dissolve in the hot alkaline solution, while clay minerals and iron pyrite are converted into acid-soluble compounds which are removed in the acid washing step. Acid also removes any carbonate minerals which are present in the coal.

In the present study the behavior of some of the principal coal minerals was traced during alkaline leaching. This was accomplished by leaching several types of coal and by leaching individual minerals, which are commonly present in coal, with various alkalis. Different alkali concentrations and temperatures were employed. The solid reaction products were characterized by x-ray diffraction (XRD) and by dissolution in mineral acids. Results achieved with Illinois No. 6 coal are discussed, since they are representative, and the results of individually leaching quartz, kaolinite, and iron pyrite

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are described because these minerals generally account for a major portion of the mineral matter in many coals.

Experimental Methods

Illinois No. 6 coal, obtained from the Elm Mine in Illinois, was dried under nitrogen at 90°C for 24 hr. and then ground to -74 μm size. Analysis of the dry coal by ASTM methods (8) revealed the following composition: 12.75% ash, 1.32% pyritic sulfur, 0.24% sulfate sulfur, 1.68% organic sulfur, and 3.24% total sulfur. Examination by XRD showed the principal mineral impurities to be iron pyrite, quartz, kaolinite, and calcite (Table I). Iron pyrite nodules were obtained from refuse produced in cleaning coal from Mahaska County, Iowa. The nodules were crushed and then ball-milled to -38 μm size; principal impurities determined by XRD are indicated in Table I. Part of the ground pyrite was treated for 1 hr. with excess 1.2 *M* hydrochloric acid at 70°C under nitrogen to remove acid-soluble impurities; it was then washed and dried. The acid-cleaned material contained 88% iron pyrite, based on total sulfur content, and significant amounts of quartz and kaolinite plus a trace of titania. In addition, the material seemed to contain a non-crystalline constituent which may have been coal. Quartz obtained for this study did not appear to contain significant amounts of any impurities when examined by XRD. On the other hand, the kaolin which was obtained seemed to contain a significant amount of quartz and trace quantities of illite and titania.

For the leaching experiments, a weighed amount of finely divided coal or mineral matter was mixed with 120 ml. of alkaline solution in a 300-ml. stainless steel (Type 316) autoclave equipped with a turbine agitator. The system was flushed with nitrogen and then heated to the desired leaching temperature. The mixture was stirred continuously while leaching was conducted at constant temperature and pressure for a specified period. After this treatment, the autoclave

Table I. Materials Which Were Chemically Treated

Material	Source	Size, μm	Impurities Indicated by XRD
Illinois			
No. 6 coal	Trivoli County (Ill.)	-74	FeS_2 , SiO_2 , kaolinite, CaCO_3
Raw pyrite	Coal, Mahaska County (Ia.)	-38	CaCO_3 , iron oxides, SiO_2 , kaolinite, TiO_2
Cleaned pyrite	Same as above	-38	SiO_2 , kaolinite, TiO_2
Quartz	Ottawa Sand (Ill.)	-38	None
Kaolin	Old Hickory No. 5 ball clay (Ky.)	-74	SiO_2 , illite, TiO_2

was cooled quickly, and the contents of the autoclave were filtered to recover any undissolved solids. The solids were washed with water, dried in an oven, weighed, and divided into two parts. One part was analyzed by XRD or other means, and the other part was treated with acid to determine the proportion of acid-soluble material. For the acid treatment step, up to 3 g. of alkali-leached material was mixed with 300 ml. of mineral acid (approximately 2 M) in a stirred, three-neck Pyrex reaction flask fitted with a reflux condenser. The treatment was conducted for 30 min. either at room temperature (25°C) or at the boiling point (100°C). After the treatment the mixture was filtered, and any undissolved solids were washed with 600 ml. of water, dried, weighed, and analyzed by XRD or other means. XRD analysis was performed with a Siemens D500 diffractometer using copper K_{α} radiation. The ash content of the treated coal was determined by ASTM Method D3174 (8), while the sulfur content was determined with a Fisher model 475 total sulfur analyzer.

Results with Coal

The results of leaching Illinois No. 6 coal with different alkaline solutions followed by acid treatment are shown in Table II. In each leaching experiment 15 g. of coal was leached with 120 ml. of alkaline solution at 250°C for 1 hr. In some experiments the alkali-leached coal was washed with hydrochloric acid, and in other experiments the coal was washed with sulfuric acid. When hydrochloric acid was employed, the acid washing step was conducted at the boiling point and the final water washing step at room temperature. However, when sulfuric acid was used, the washing steps were conducted at various temperatures to study the temperature effect.

Table II. Results of Treating Illinois No. 6 Coal with a Hot Alkaline Solution Followed by Acid Leaching

Alkali Trtmt.		Acid Trtmt.		Washing	Product, %			Reduction, %	
Type	M	Type	T., °C	T., °C	Yld. ^a	Ash ^b	S _t ^a	Ash ^b	S _t ^a
NaHCO ₃	2.0	HCl	100	25	95	6.57	3.14	48	15
Na ₂ CO ₃	1.0	HCl	100	25	94	2.61	2.40	80	35
NaOH	2.0	HCl	100	25	83	1.28	1.95	90	47
Na ₂ CO ₃	1.0	H ₂ SO ₄	25	25	94	3.40	2.72	73	27
Na ₂ CO ₃	1.0	H ₂ SO ₄	100	25	94	3.26	3.09	74	17
Na ₂ CO ₃	1.0	H ₂ SO ₄	100	100	94	2.93	2.55	77	31

^aYield and total sulfur content on a dry, ash-free basis

^bAsh content on a dry basis

The results of the coal leaching experiments indicate that the ash and total sulfur contents of the coal were reduced substantially while the product yield was generally high. The results were affected by the type of alkali, and the effectiveness of the alkali decreased in the following order: $\text{NaOH} > \text{Na}_2\text{CO}_3 > \text{NaHCO}_3$. Although the greatest reduction in ash and sulfur contents was realized with sodium hydroxide, the product yield (84%) was the lowest. The 47% reduction in total sulfur content achieved with sodium hydroxide was equivalent to the reduction which would have been realized if all of the inorganic sulfur had been removed and none of the organic sulfur. Sodium carbonate appeared to be only slightly less effective than sodium hydroxide in reducing the sulfur and ash contents of the coal, but it provided a greater yield (94%). Sodium bicarbonate appeared considerably less effective than the other alkalis. For coal leached with sodium carbonate, slightly lower ash and sulfur contents were obtained when the material was washed with hydrochloric acid than when it was washed with sulfuric acid. However, the effectiveness of the sulfuric acid treatment was improved by using hot acid and by using hot water instead of cold water to wash the acid-treated coals.

Results with Individual Minerals

To explain the preceding results with coal, a series of leaching experiments was carried out with individual minerals. In the first set of experiments, $-38\ \mu\text{m}$ size quartz particles were leached with various hot alkaline solutions to study the effects of alkali type, alkali concentration, ratio of alkali to quartz, temperature, and leaching time on dissolution. After each leaching, the reactor contents were filtered with Whatman No. 40 filter paper using suction, and the residue was washed with cold water, dried at 350°C for 2 hr., and weighed. The percentage of material extracted was calculated using the following expression:

$$\text{Extraction (\%)} = 100 - \frac{\text{wt. of residue}}{\text{wt. of feed}} \times 100 \quad (1)$$

The results of leaching quartz with sodium carbonate solutions having different concentrations are shown in Figure 1. For each point, 2.0 g. of quartz was leached with 120 ml. of solution at 250°C for the indicated time. It can be seen that the amount of material extracted increased linearly with time for about the first hour. During this period the rate of extraction also increased with alkali concentration to approximately the 0.5 power. Following the constant rate period, no further material was extracted. Apparently the solubility limit was reached, and it seemed to be the solubility limit at room temperature rather than at the leaching temperature. The following evidence pointed to the lower temperature limit. The residue remaining after leaching quartz for 2 hr. or more was an amorphous, non-crystalline solid which was insoluble in hot hydrochloric acid. Examination of the residue for various chemical elements by energy dispersive x-ray analysis revealed a high concentration of silicon and only a trace of sodium. The results suggested that quartz had dissolved in the hot solution, and upon cooling some of the silica had reprecipitated as an amorphous or

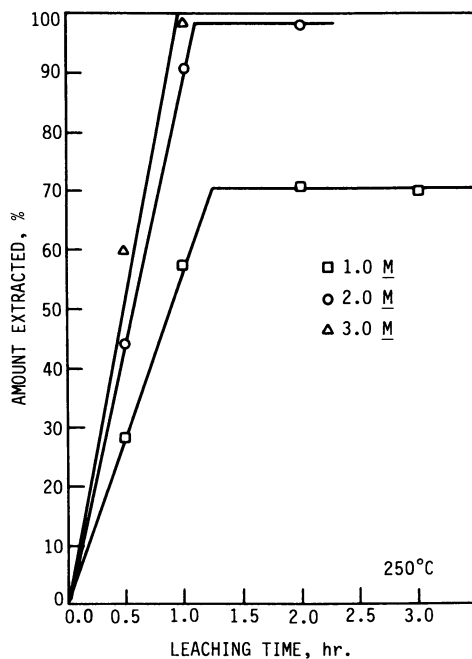


Figure 1. Dissolution of quartz (2.0 g.) by hot sodium carbonate solutions (120 ml.) having different concentrations.

glassy material. On the other hand, the residue remaining after quartz had been leached for less than 1 hr. appeared to be largely unreacted quartz. Furthermore, when quartz was leached for 1 hr. at the higher temperature of 300°C with a 1.0 M sodium carbonate solution, the amount of material extracted was only 69% which was no greater than the maximum amount extracted at 250°C. From published solubility data (9) for silica in various alkaline solutions, one would expect the solubility of quartz in a sodium carbonate solution to increase markedly with temperature.

Even though the amount of silica extracted seemed to be limited by the room temperature solubility limit, this limit was raised by increasing either the alkali concentration or the ratio of alkali to quartz. Thus by increasing the sodium carbonate concentration from 1.0 M to 2.0 M, the maximum amount extracted was raised from 70% to 98.5%. Moreover, when the quantity of quartz leached for 1 hr. with a 1.0 M solution at 250°C was reduced from 2 g. to 1 g., the percentage extracted increased from 58% to 95%.

Quartz was also leached for 1 hr. at 250°C with 2.0 M solutions of either sodium hydroxide or sodium bicarbonate. In each case 2.0 g. of quartz was leached with 120 ml. of solution. Most of the quartz (99.5%) was converted to soluble sodium silicates and extracted by the hot sodium hydroxide solution. On the other hand, only 10% of the quartz was extracted by the sodium bicarbonate solution, and the residue appeared to be entirely quartz. These values were noticeably different from the 58% extracted by 1.0 M sodium carbonate under similar conditions. Therefore, these solutions were not equivalent in leaching ability even though each provided the same number of moles of sodium. None of the residues remaining after leaching quartz with any of the alkalis were acid-soluble.

In a second set of experiments, -74 μ m size kaolin particles were leached with hot alkaline solutions to study the conversion of kaolinite to various sodium hydroaluminosilicate compounds (Table III) under different leaching conditions. In each experiment, 15 g. of kaolin was leached with 120 ml. of alkaline solution. The solid reaction product was recovered by filtration, washed with water, dried in an oven at 95°C, and analyzed by XRD. Although this method of analysis identified the minerals present, it could provide only an approximate indication of the relative proportions of the various minerals present. The amount of quartz was particularly difficult to assess because the method of detection was very sensitive to this mineral. Therefore, the results are reported only in terms of major, minor, and trace quantities present in the product as indicated by XRD (Table IV). Because the small amount of titania in the kaolin was apparently not affected by even the most rigorous leaching conditions, the product always contained a trace of this material and no further mention seems necessary.

When kaolin was leached with 1.0 M sodium carbonate at 200°C for 1 hr., most of the kaolinite was converted to the sodalite-type natrodavyne (NS) while the quartz and illite impurities were not affected noticeably (Table IV). Increasing the leaching temperature to 250°C resulted in the conversion of the kaolinite to a mixture of mixed-type natrodavyne (NCS) and analcime (A) and complete dissolution of the quartz impurity. The illite impurity was not affected. Leaching at 300°C and above resulted in the conversion of the

Table III. Various Sodium Hydroaluminosilicates Produced in Leaching Kaolinite with Hot Alkaline Solutions

Mineral	Chemical formula	Symbol
Analcime	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4(\text{SiO}_2) \cdot 2(\text{H}_2\text{O})$	A
Hydroxycancrinite	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2(\text{SiO}_2) \cdot \frac{2}{3}(\text{NaOH}) \cdot n(\text{H}_2\text{O})$	HC
Hydroxysodalite	(same as above)	HS
Natrodavyne (sodalite-type)	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2(\text{SiO}_2) \cdot \frac{1}{3}(\text{Na}_2\text{CO}_3) \cdot n(\text{H}_2\text{O})$	NS
Natrodavyne (cancrinite-type)	(same as above)	NC
Natrodavyne (mixed type)	(same as above)	NCS

kaolinite to the cancrinite-type natrodavyne (NC). Only at 350°C did the illite impurity appear to be affected.

A similar trend was observed when kaolin was leached for 1 hr. at 250°C with sodium carbonate solutions of different concentrations (Table IV). At the lowest concentration (0.2 M), part of the kaolinite was converted to the sodalite-type natrodavyne while the impurities were untouched. At the highest concentration of sodium carbonate (2.0 M), the kaolinite was converted to the cancrinite-type natrodavyne, and although the quartz was extracted, the illite remained.

Somewhat similar changes were observed when the leaching time was varied while holding the concentration of sodium carbonate at 1.0 M and the temperature at 250°C. With a leaching time of 0.5 hr. the kaolinite was converted to a mixture of analcime and sodalite-type natrodavyne, whereas with a leaching time of 2.0 hr. the kaolinite was largely converted to the cancrinite-type natrodavyne. Not all of the quartz was extracted when leaching was conducted for 0.5 hr., but all of the quartz appeared to be removed when leaching was conducted for longer periods. However, the illite remained even after 2 hr. of leaching.

When kaolin was leached with 1.0 M sodium hydroxide at 250°C for 1 hr., most of the kaolinite appeared to be converted to analcime (Table IV). Increasing the concentration to 2.0 M resulted in converting most of the kaolinite to hydroxycancrinite (HC). In either case the quartz impurity was extracted but the illite impurity remained. Leaching kaolin with 2.0 M sodium bicarbonate at 250°C for 1 hr. converted the kaolinite to the sodalite-type natrodavyne, but it had no apparent effect on the impurities.

To investigate the dissolution of the sodium hydroaluminosilicates produced by alkaline leaching, 3.0 g. portions of the leached product were treated with 300 ml. of acid in a stirred flask for 30 min. Either 2.0 M hydrochloric acid or 1.8 M sulfuric acid was utilized. While hydrochloric acid was always used at the boiling point, sulfuric acid was sometimes used at the boiling point and sometimes at room temperature. From XRD analysis of the solid

Table IV. Results of Leaching 15 g. Kaolin with 120 ml. Alkaline Solution

Leaching conditions				Mineral products excluding TiO_2 , type, (amount) ^a
Alkali	M	°C	hr.	
Na_2CO_3	1.0	200	1.0	NS(maj), SiO_2 (maj), kaolinite(min), illite(tr)
Na_2CO_3	1.0	250	1.0	NCS(maj), A(maj), illite(tr)
Na_2CO_3	1.0	300	1.0	NC(maj), A(min), illite(tr)
Na_2CO_3	1.0	350	1.0	NC(maj)
Na_2CO_3	0.2	250	1.0	SiO_2 (maj), kaolinite(min), NS(min) illite(tr)
Na_2CO_3	0.5	250	1.0	SiO_2 (maj), NS(maj), illite(tr)
Na_2CO_3	1.0	250	1.0	NCS(maj), A(maj), illite(tr)
Na_2CO_3	2.0	250	1.0	NC(maj), illite(tr)
Na_2CO_3	1.0	250	0.5	A(maj), NS(maj), SiO_2 (min), illite(tr)
Na_2CO_3	1.0	250	1.0	NCS(maj), A(maj), illite(tr)
Na_2CO_3	1.0	250	2.0	NC(maj), A(min), illite(tr)
NaOH	1.0	250	1.0	A(maj), HS(min), illite(tr)
NaOH	2.0	250	1.0	HC(maj), A(min), illite(tr)
NaHCO_3	2.0	250	1.0	NS(maj), SiO_2 (maj), illite(tr)

^a Amount: maj = major quantity, min = minor quantity, tr = trace quantity

residue remaining after the acid treatment, it was found that all of the sodalite-type and cancrinite-type compounds were dissolved by the acids whether hot or cold. On the other hand, analcime was completely dissolved only by the boiling acids.

In a third set of experiments, $-38\text{ }\mu\text{m}$ pyrite particles were leached with hot alkaline solutions to study the conversion of iron pyrite to iron oxide and soluble sulfur species. In each experiment, 5 g. of acid-cleaned pyrite was leached with 120 ml. of alkaline solution for 1 hr. In addition to analyzing the solid residue by XRD, the total sulfur content of the leachate was determined in order to estimate pyrite conversion.

When pyrite was leached for 1 hr. with 1.0 *M* sodium carbonate at 250°C , only 12.7% of the pyrite was converted to iron oxide and soluble sulfur species (Table V). Increasing the leaching temperature to 300°C raised the conversion to 26.4%, and increasing the temperature to 350°C raised the conversion to 44.8%. In each case the solid residue consisted principally of hematite and unreacted pyrite.

Increasing the sodium carbonate concentration, while maintaining the leaching time at 1 hr. and temperature at 250°C , increased the pyrite conversion only slightly (Table V). On the other hand, when pyrite was leached with 2.0 *M* sodium hydroxide at 300°C for 1 hr., a conversion of 62% was achieved. Again, hematite appeared to be the principal solid reaction product.

When the pyrite residue from the alkaline leaching step was treated with acid, all of the hematite dissolved in either hot hydrochloric acid or hot sulfuric acid. However, the hematite appeared to dissolve incompletely or very slowly in cold sulfuric acid. Unreacted pyrite was not touched by the acids whether hot or cold.

Behavior of Mineral Matter During Coal Leaching

Following the preceding experiments with individual minerals, further consideration was given to the behavior of the mineral matter in coal

Table V. Results of Leaching 5 g. Acid-cleaned Pyrite with 120 ml. Alkaline Solution for 1 hr.

Alkali	Leaching conditions		Conv., %	Residue
	Conc., <i>M</i>	Temp., $^{\circ}\text{C}$		
Na_2CO_3	1.0	250	12.7	FeS_2 , Fe_2O_3
Na_2CO_3	1.0	300	26.4	FeS_2 , Fe_2O_3
Na_2CO_3	1.0	350	44.8	FeS_2 , Fe_2O_3
Na_2CO_3	1.0	250	12.7	FeS_2 , Fe_2O_3
Na_2CO_3	2.0	250	14.5	----
Na_2CO_3	3.0	250	15.8	----
NaOH	2.0	300	62.0	FeS_2 , Fe_2O_3

itself during leaching. The coal was examined by XRD after both the alkaline leaching step and the acid/water washing step. Leaching Illinois No. 6 coal with 2 M sodium bicarbonate at 250°C for 1 hr. appeared to convert essentially all of the kaolinite to natrodavyne and analcime and a small portion of the iron pyrite to hematite while not greatly affecting the quartz and calcite. However, it appeared that some of the quartz was converted to analcime since this mineral has a higher ratio of silica to alumina than is present in kaolinite. Following the subsequent acid washing step, the remaining mineral matter consisted mostly of quartz and pyrite. Leaching Illinois No. 6 coal with 1 M sodium carbonate under similar conditions also converted the kaolinite to natrodavyne and analcime and part of the pyrite to hematite; the quartz was either converted to soluble sodium silicates or analcime. After washing the alkali-treated coal with acid, pyrite seemed to constitute most of the remaining mineral matter. Leaching Illinois No. 6 coal with 2 M sodium hydroxide at 250°C for 1 hr. seemed to convert all of the kaolinite to hydroxycancrinite and a large portion of the pyrite to hematite; most of the quartz was extracted or converted. After washing the coal with acid, only a small amount of pyrite remained. These results were generally in good agreement with those observed in the leaching of individual minerals.

Conclusions

Most of the mineral matter was removed from a representative coal (Illinois No. 6) by first leaching the finely ground material with a hot alkaline solution and then washing the product with a mineral acid and water. The effectiveness of various alkalis for converting or extracting mineral matter decreased in the following order: $\text{NaOH} > \text{Na}_2\text{CO}_3 > \text{NaHCO}_3$. Coal recovery, on the other hand, increased in the same order. Examination of the coal by XRD after each step and a study of the behavior of individual minerals when subjected to the same treatment indicated good agreement in results. In other words, the results were generally similar regardless of whether the minerals were leached individually or in a mixture with coal. The results of leaching several of the most prevalent minerals in coal on an individual basis are summarized below.

It was shown that fine-size quartz particles readily dissolve in 1-2 M sodium carbonate or sodium hydroxide at 250°C. However, when quartz is extracted by a hot solution which is then cooled, an amorphous, acid-insoluble material is produced under some conditions. A likely possibility is that amorphous silica precipitates when the room temperature solubility limit of the material is exceeded. Formation of the amorphous material is prevented by using higher concentrations of alkali or a higher ratio of alkali to silica.

It was also shown that kaolinite reacts with hot alkaline solutions to form various sodium hydroaluminosilicates which are acid-soluble. The particular sodium hydroaluminosilicate formed depends on the type of alkali employed, the alkali concentration, the treatment temperature, and length of treatment. When sodium carbonate is employed, kaolinite is largely converted to the sodalite-type natrodavyne under less rigorous conditions and to the cancrinite-type natrodavyne under more rigorous conditions. Under intermediate

treatment conditions, the mixed-type natrodavyne and analcime are produced. When sodium hydroxide is employed, kaolinite is largely converted to analcime and hydroxycancrinite with the latter being favored by higher alkali concentrations.

It was further shown that iron pyrite reacts with hot alkaline solutions to form hematite and soluble sulfur species. Sodium hydroxide is considerably more effective than sodium carbonate for this reaction. However, the effectiveness of sodium carbonate solutions can be increased by increasing the treatment temperature and to a lesser extent by increasing the alkali concentration. The hematite produced is readily dissolved by hot mineral acids.

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