

## OXIDATIVE POWER OF SMECTITES MEASURED BY HYDROQUINONE

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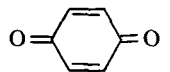
**Abstract**—The oxidative power of a smectite can be measured quantitatively by oxidation of hydroquinone to *p*-benzoquinone in a clay slurry. Oxidation takes place in the presence of O<sub>2</sub> (air) but not N<sub>2</sub> unless Fe<sup>3+</sup> or Cu<sup>2+</sup> are the exchangeable cations. This study examined 26 smectite samples with varying compositions and processing. The oxidative power increases with decreasing Li-fixation and increasing cation exchange capacity. Li-fixation does not depend upon the tetrahedral Al. The cation exchange capacity can decrease markedly by mere storage in water.

The oxidation proceeds principally on the surface by adsorbed oxygen molecules or radicals. A mechanism is proposed. With Fe<sup>3+</sup> or Cu<sup>2+</sup> present, even under N<sub>2</sub>, oxidation occurs via electron transfer. With smectites containing Fe<sup>2+</sup>, both the Fe and the hydroquinone are oxidized in the same reaction.

### INTRODUCTION

VERY FEW studies have been concerned with the influence of clay minerals on the alteration of organic materials. Today it would be especially interesting to study how clay minerals alter materials found in waste water, such as phenolic and humic substances (Eisenhauer, 1967). Some products resulting from the reductive degradation of humic substances are derivatives of polyhydric phenols, such as pyrocatechol, pyrogallol, and hydroquinone (Burgess *et al.*, 1964; Ziechmann, 1964; Dubach *et al.*, 1964).

Several workers (Nierenstein, 1915; Feifer *et al.*, 1959; Kaiser and Weidman, 1965; Weidman and Kaiser, 1966) have studied the oxidation of polyhydric phenols with a variety of oxidizing agents. The oxidation of hydroquinone produces a well-defined monomeric product, *p*-benzoquinone,



whereas the oxidation of many other polyhydric phenols gives rise to products which are dimers or polymers of ill-defined composition. Thus, a detailed study involving the oxidation of hydroquinone by clays promised to shed light on the interactions, with minimum side effects.

Goodman and Siegel (1959) demonstrated the effect of solids on the oxidation of pyrogallol, a trihydric phenol. They found a 3-fold increase in the amount of oxidized product when cellulose (filter paper) was present in the reaction mixture. The increase in yield was shown by comparing the

optical densities of two samples, one of which contained cellulose during the reaction. This work pointed out that an apparently inert surface may have a profound effect on some chemical reactions. Studies involving the polymerization of organic monomers in the presence of clay minerals have been carried out by Friedlander (1963), Solomon and Roser (1965), Solomon and Swift (1967) and Solomon and Loft (1968). They emphasize that clay minerals cannot be considered to be inert or important only as adsorbents. Blumstein (1965a) observed that higher doses of X-rays and higher concentrations of free radical catalysts were required to initiate polymerization of clay-monomer complex than for polymerization of the bulk monomer. Blumstein (1965b) also found that the polymer inserted between the layers of montmorillonite was more resistant to thermal degradation than was the external polymer. These studies show that clay minerals can both activate chemical reactions and stabilize them.

Recently, Solomon *et al.* (1968) have demonstrated the influence of clay minerals on the oxidation of organic compounds, particularly the oxidation of benzidine to benzidine-blue, brought about by the introduction of montmorillonite. They proposed that the aluminum atoms exposed at the edges of the crystal and the transition metal atoms in the higher oxidation states present in the clay minerals are the active sites which bring about chemical reactions. This study will be discussed in considerable detail later in this paper.

The present work employed a u.v. spectrophoto-

metric method to determine quantitatively the amount of *p*-benzoquinone formed from hydroquinone in the presence of various clay minerals, with a view to determining the possible role of 4-fold or 6-fold aluminum or Fe<sup>3+</sup>, or of other constituents in the clay.

#### EXPERIMENTAL

##### *Preparation of the montmorillonites*

The various clays, including both 'oxidized' (yellow) and 'reduced' (red) bentonites, used in this investigation are listed in Table 1. Georgia Kaolin Company supplied most of the 26 samples used in this investigation. Additional clays include a hectorite from Hector, California, three montmorillonites ('Volclay') from American Colloid Company and a synthetic montmorillonite from Charles Pfizer and Company. Chemical analyses for seven samples are given in Table 3.

The clays were initially saturated by sodium or lithium ions by treating them three times for 24 hr each with 1N chloride solutions. They were then washed with deionized water by dialysis at 60°C. until a negative Cl<sup>-</sup> test was obtained, after which

the water was changed three more times. The Na-ane Li- clays were fractionated to give < 1 μm particle size material in order to remove mineral impurities. Some of the clays had been dried before slurring and saturation; others had not. This drying can be of extreme importance.

Other cation-saturated montmorillonites were prepared by taking aliquots of the various Na-clays and treating them with the appropriate 1N chloride solutions in the same fashion as the initial saturations. The Fe<sup>3+</sup> and Cu<sup>2+</sup> saturated forms of Gelwhite® L and the Fe<sup>3+</sup> of Mineral Colloid-BP were washed by centrifugation in deionized water at room temperature in order to minimize the formation of hydroxy material.

Most clay suspensions were freshly prepared. However, to examine the effect of extended periods in water, some suspensions were allowed to age 3 months, 6 months, or 1 yr.

##### *Cation exchange capacities*

Cation exchange capacities were determined by first exchanging the Li- and Na- clay five times with 1N CaCl<sub>2</sub>. Next, without removing the excess

Table 1. Locations of the smectite samples

1.	K-4 Midwest Wyoming, Steele formation. Had been dried and pulverized in plant
2.	K-4 Foundry – Similar 1, but never dried
3.	Synthetic Clay – Synthetic montmorillonite from Chas. Pfizer and Company
4.	K-2 Brock – Kaycee, Wyoming, Mowry formation. Had been dried and pulverized in plant
5.	Gelwhite L – Gonzales, Texas, Jackson group. (white bentonite) Had been water dispersed with (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> and TSPP, centrifuged to < 2 μm, and dried in plant
6.	Bates Hole – Bates Hole area (Natrona County) Wyoming, Mowry formation. Had been dried and pulverized in plant
7.	Bates Hole No. 2 – Collected from pit in source area of No. 6, never allowed to dry
8.	Mineral Colloid BP – Bates Park area (Natrona County) Wyoming, Mowry formation. Had been water dispersed with Calgon, centrifuged to < 2 μm, and dried in plant
9.	Helms Colloid – Gonzales, Texas, Jackson group (white bentonite). Had been water dispersed without chemicals, centrifuged to < 2 μm, and dried in plant
10.	Syler – Muldoon, Texas, Jackson group (yellow bentonite). Had been dried and pulverized in plant
11.	Newcastle Brown – Colony, Wyoming, Newcastle formation Collected from pit, air dried
12.	Volclay No. 1 – Wyoming bentonite solid by American Colloid Company
13.	Hectorite – Newberry Springs, California Unprocessed sample, air dried
14.	Bates Park prior 1966 – Bates Park area (Natrona County, Wyoming), Mowry formation. Mined before 1966 and stockpiled. Collected from stockpile.
15.	Newcastle Green – Similar to No. 11, but green in color
16.	K-2 Blue – Kaycee, Wyoming, Mowry formation. Collected from pit, never dried
17.	K-2 Good – Similar to No. 16, but yellow
18.	Bates Park 1966 – Similar to No. 14, but mined and stockpiled in 1966
19.	Plattensburg – Plattensburg Bay area, South Africa
20.	Gelwhite L No. 2 – Similar to No. 5, but had remained in deionized water one year before oxidation experiment
21.	Volclay No. 2 – Wyoming bentonite from American Colloid Company
22.	Bates Park South Assessment – Bates Park area (Natrona County) Wyoming, Mowry formation. Collected from stockpile of abandoned assessment pit, never dried.
23.	Bates Park Blue – Similar to No. 18, but blue in color
24.	Fuller Earth – Twiggs County, Georgia, Tuscaloosa formation. Collected from pit wall
25.	Bates Hole No. 1 – Similar to No. 7, but from another pit
26.	Volclay No. 3 – Wyoming bentonite sold by American Colloid Company

CaCl<sub>2</sub> solution the clays were washed five times with 1N ammonium acetate. Washings were collected and the total Ca<sup>2+</sup> determined by EDTA titration. The excess CaCl<sub>2</sub> solution entrained by the clay determined by density measurements and this excess Ca<sup>2+</sup> deducted from the results (Okazaki, Smith and Moodie, 1962).

Time studies disclosed that mere aging in water can fix Li<sup>+</sup>; i.e., make it unexchangeable with Ca<sup>2+</sup> by the above method. This fixed Li<sup>+</sup> was removed in the following manner. First, the aged Li-clay was treated once with 0.1M tartaric acid (a chelating agent). Next, it was treated three times with 1N CaCl<sub>2</sub>, then washed free of Cl<sup>-</sup>. The exchange capacity was then established by washing with NaCl and titrating the Ca<sup>2+</sup> in the washings with EDTA.

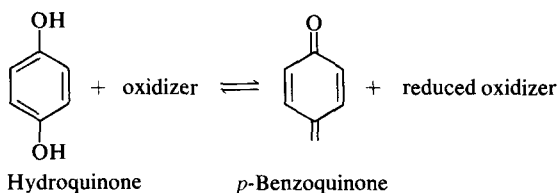
In a modification of the Li test of Greene-Kelly (1955), the fresh Li-clays were heated at 250°C. for 16 hr. Then, not only was the exchange capacity determined as in the first paragraph, but also the amount of Li<sup>+</sup> displaced by Ca<sup>2+</sup>. Li-fixation, according to Greene-Kelly (1955), Schultz (1969) and others, can establish the beidellitic character of various smectites. Beidellitic character expresses the amount of aluminum in the tetrahedral layer and thus any importance of tetrahedral aluminum (including that on the crystal edge) in chemical reactions.

#### Surface area

The methylene blue adsorption techniques of Brindley and Thompson (1970) provided the surface area data. The maximum flocculation point during increasing methylene blue addition is assumed to be the total external surface coverage.

#### Oxidation reactions

The reaction in its simplest form is:



The hydroquinone was obtained from Fisher Scientific Company. U.V. spectrophotometry demonstrated purity of 99 + per cent.

To 10 ml of 20.0 mM aqueous solution of hydroquinone, 10 ml of clay suspension (10 g 100°C. dry clay/1.) and 10 ml of deionized water were combined to give a final volume of 30 ml.

For the hydroquinone reference solutions, 10 ml of 20.0 mM aqueous hydroquinone was combined with 20 ml of deionized water. For the *p*-benzoquinone reference solutions, 10 ml of the hydroquinone stock solution, 10 ml of 40.0 mM AgNO<sub>3</sub> and 10 ml of deionized water were combined. The AgNO<sub>3</sub> oxidized the hydroquinone completely to *p*-benzoquinone. Additional experiments used a 3.0 mM rather than the 20.0 mM hydroquinone solution to check concentration effects.

For oxidation, air was bubbled through each sample for 18 hr. Some samples were reacted 4 and 108 hr, thereby gaining some idea of the reaction rate. Further, the 108 hr period would establish if the reactions were essentially complete after 18 hr. If not, then these experiments could measure the ability of the clays to alter reaction rates rather than their ability to oxidize. To determine if oxidation occurred in the absence of oxygen, oxygen-free nitrogen was bubbled through the samples for 18 hr.

The oxidation of hydroquinone is pH dependent. To check the effect of pH, air was bubbled for 18 hr through hydroquinone in water at pH values ranging from 4–10. Only at pH 9 did any discernible oxidation begin to occur. Appreciable oxidation occurred at pH 10. The clay slurries were all initially pH 6.7 ± 0.2, safely below the range of pH-induced effects. During reaction with clay present, the pH tended to move lower, thereby never entering the range of pH effects. Buffering agents were not used, owing to the danger of aggregating the clay or modifying the surface.

After treatment, the samples were diluted to 100 ml. in volumetric flasks using a pH 2 buffer solution. The clay was centrifuged down using a Sorvall SS-1 supercentrifuge. Aliquots of 5 ml of the supernatant solutions were diluted to the mark in 50 ml volumetric flasks with HCl-KCl pH 2 buffer. A Beckman DK-2A spectrophotometer recorded the u.v. spectra between 3600 and 2200 Å. The adsorption band of hydroquinone occurs at 2920 Å, that of *p*-benzoquinone at 2460 Å. Figure 1 gives the spectra and indicates that the hydroquinone and *p*-benzoquinone absorption bands are sufficiently resolved to enable quantitative measurements of each. Because of possible side reactions and adsorption of hydroquinone by the clay, both the *p*-benzoquinone generated and the hydroquinone depleted were measured. Sadtler Standard Spectra (1970) gives the necessary u.v. absorption maxima and molar extinction coefficients for both hydroquinone and *p*-benzoquinone. The sum of *p*-benzoquinone plus remaining hydroquinone

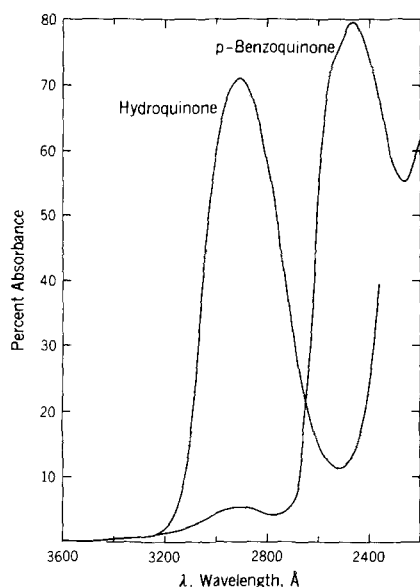


Fig. 1. U.V. spectra of hydroquinone and *p*-benzoquinone in a KCl/HCl pH 2 buffer.

should equal the initial hydroquinone concentration. Any deficiency would arise from hydroquinone adsorption by the clay or perhaps polymerization of the monomer. The summation of the amounts of hydroquinone and *p*-benzoquinone were compared to the initial concentration for some blue montmorillonites, which can be oxidized under alkaline conditions to the yellow form, and the yellow montmorillonites. The two forms were found to behave differently.

#### Reflectance spectroscopy

The reflectance spectra of Cu (II)-montmorillonite and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were obtained using a Beckman DK-2A spectrophotometer with a reflectance attachment. The spectrum of Cu (II)-montmorillonite, dried at  $100^\circ\text{C}$ , is compared to that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Figure 2 indicates the similarities of the two curves.

#### RESULTS

The amounts of *p*-benzoquinone formed as a result of the interaction of hydroquinone with various montmorillonites are given in Table 2. The extent of oxidation is expressed as m-equiv. *p*-benzoquinone per 100 g dry clay and is determined by measuring the increase in optical density at  $2460 \text{ \AA}$  for reaction systems containing clay. The blue montmorillonites show the increase in absorbance at  $2460 \text{ \AA}$ , but also have an increase in optical density in the region greater than  $3000 \text{ \AA}$ .

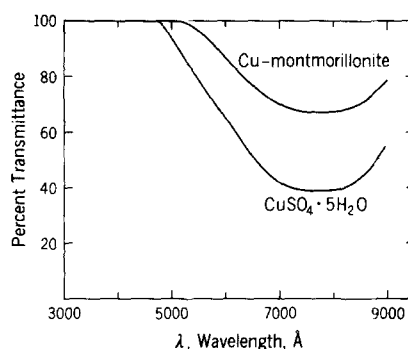


Fig. 2. Reflectance spectra of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and a  $\text{Cu}^{2+}$ -saturated montmorillonite.

The observed spectral changes for the yellow and blue montmorillonites are shown in Fig. 3.

#### Effects of aluminum and iron content on the oxidizing power of clay

Table 4 compares the amounts of *p*-benzoquinone

Table 2. Effect of smectites on the oxidation of hydroquinone

Montmorillonite		m-equiv/100 g <i>p</i> -Benzoquinone	
		(1)	(2)
1.	K-4	25.5	46.5
2.	K-4 Foundry	22.1	
3.	Synthetic Clay	15.0	
4.	K-2	13.5	24.6
5.	Gelwhite L	13.4	24.4
6.	Bates Hole	12.7	23.2
7.	Bates Hole No. 2	12.1	
8.	Mineral Colloid BP	11.4	20.8
9.	Helms Colloid	9.6	
10.	Syler	9.3	
11.	Newcastle Brown	9.3	
12.	Volclay No. 1	8.8	
13.	Hectorite	8.8	
14.	Bates Park prior 1966	8.6	
15.	Newcastle Green	7.4	
16.	K-2 Blue	7.4	
17.	K-2 Good	7.1	
18.	Bates Park 1966	6.6	
19.	Plattensburg	5.5	
20.	Gelwhite L No. 2	5.5	
21.	Volclay No. 2	5.0	
22.	Bates Park South Assessment	4.7	
23.	Bates Park Blue	4.5	
24.	Fullers Earth	4.0	
25.	Bates Hole No. 1	3.7	
26.	Volclay No. 3	3.4	

1—The starting concentration of Hydroquinone was 3.0 mM. for the 26 clays.

2—The starting concentration of Hydroquinone was 20.0 mM.

Table 3a. Chemical analyses and structural formulae of seven montmorillonites

% Oxide	(6) Bates Hole	(4) K K-2	(1) K-4	(8) Mineral Colloid BP	(5) Gelwhite L	(26) Volclay No. 3	(13) Hectorite
SiO <sub>2</sub>	54.0	61.7	56.7	60.2	64.8	61.3	54.0
Al <sub>2</sub> O <sub>3</sub>	22.4	17.8	18.3	22.9	20.5	22.4	N.D.
Fe <sub>2</sub> O <sub>3</sub>	3.65	3.29	4.29	4.61	0.69	3.55	0.036
FeO	0.24	0.48	0.56	0.31	0.16	0.39	0.07
TiO <sub>2</sub>	0.054	0.097	0.49	0.18	0.26	0.11	0.042
CaO	0.87	1.91	2.52	N.D.	N.D.	N.D.	2.02
MgO	2.11	2.07	3.28	2.67	3.97	2.81	25.0
Na <sub>2</sub> O	0.025	0.027	0.066	2.86	2.93	2.71	0.01
K <sub>2</sub> O	0.30	0.06	0.09	0.11	0.044	0.044	0.05
Li <sub>2</sub> O	2.80	0.99	1.1	N.D.	N.D.	N.D.	3.60
H <sub>2</sub> O <sub>550</sub>	10.2	8.03	9.41	1.37	1.76	1.27	10.6
H <sub>2</sub> O <sub>1050</sub>	3.84	3.65	3.69	4.66	3.90	4.55	4.66
Total	100.49	100.10	100.50	99.87	99.09	99.13	100.09

Table 3b. Structural formula

Sample	VI-Fold	IV-Fold	Exchangeable Ions	Fixed Ions	Oxygen Hydroxides
(6) Bates Hole	Fe <sub>0.38</sub> <sup>3+</sup> Fe <sub>0.03</sub> <sup>2+</sup> Mg <sub>0.44</sub> Al <sub>2.89</sub>	Si <sub>7.87</sub> Al <sub>0.13</sub>	Li <sub>0.62</sub>	Ca <sub>0.15</sub> Li <sub>0.95</sub>	O <sub>20</sub> (OH) <sub>4</sub>
(4) K-2	Fe <sub>0.33</sub> <sup>3+</sup> Fe <sub>0.05</sub> <sup>2+</sup> Mg <sub>0.41</sub> Al <sub>2.46</sub>	Si <sub>8.17</sub>	Li <sub>0.18</sub>	Ca <sub>0.27</sub> Li <sub>0.35</sub>	O <sub>20</sub> (OH) <sub>4</sub>
(1) K-4	Fe <sub>0.44</sub> <sup>3+</sup> Fe <sub>0.06</sub> <sup>2+</sup> Mg <sub>0.67</sub> Al <sub>2.69</sub>	Si <sub>7.78</sub> Al <sub>0.22</sub>	Li <sub>0.23</sub>	Ca <sub>0.37</sub> Li <sub>0.37</sub>	O <sub>20</sub> (OH) <sub>4</sub>
(8) Mineral Colloid BP	Fe <sub>0.44</sub> <sup>3+</sup> Fe <sub>0.03</sub> <sup>2+</sup> Mg <sub>0.43</sub> Al <sub>3.10</sub>	Si <sub>7.61</sub> Al <sub>0.39</sub>	Na <sub>0.73</sub>	Mg <sub>0.08</sub>	O <sub>20</sub> (OH) <sub>4</sub>
(5) Gelwhite L	Fe <sub>0.06</sub> <sup>3+</sup> Fe <sub>0.02</sub> <sup>2+</sup> Al <sub>3.07</sub> Mg <sub>0.75</sub>	Si <sub>8.10</sub>	Na <sub>0.72</sub>		O <sub>20</sub> (OH) <sub>4</sub>
(26) Volclay No. 3	Fe <sub>0.33</sub> <sup>3+</sup> Fe <sub>0.03</sub> <sup>2+</sup> Mg <sub>0.51</sub> Al <sub>3.14</sub>	Si <sub>7.78</sub> Al <sub>0.22</sub>	Na <sub>0.67</sub>		O <sub>20</sub> (OH) <sub>4</sub>
(13) Hectorite	Fe <sub>0.01</sub> <sup>2+</sup> Mg <sub>4.98</sub> Li <sub>1.01</sub> <sup>+</sup>	Si <sub>7.67</sub> Mg <sub>0.33</sub>	Li <sub>1.01</sub>	Ca <sub>0.31</sub> Li <sub>0.04</sub>	O <sub>20</sub> (OH,F) <sub>4</sub>

Table 4. Relationship of Al<sup>VI</sup>, Al<sup>IV</sup>, and Fe<sup>3+</sup> (determined from chemical analyses) content and the amount of *p*-benzoquinone formed

	Montmorillonite	<i>p</i> -Benzoquinone	Al <sup>IV</sup>	Al <sup>VI</sup>	Fe <sup>3+</sup>	Li <sub>250</sub> CEC
1.	K-4	25.5	0.22	2.69	0.44	83
3.	Synthetic	15.0	0.00	0.00	0.00	
4.	K-2	13.5	0.00	2.76	0.33	74
5.	Gelwhite L	13.4	0.00	3.07	0.06	55
6.	Bates Hole	12.7	0.63	2.89	0.38	50
8.	Mineral Colloid BP	11.4	0.39	3.10	0.44	47
13.	Hectorite	8.8	0.00	0.00	0.01	103
26.	Volclay No. 3	3.4	0.22	3.14	0.33	26

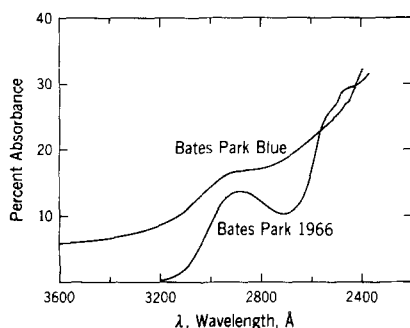


Fig. 3. U.V. spectra of hydroquinone after interaction with a reduced montmorillonite (blue Bates Park) and an oxidized montmorillonite (Bates Park, 1966).

formed by the eight clays with the total aluminum, the aluminum in 4-fold coordination and 6-fold coordination, and the ferric iron content. The amount of aluminum for each of the clays is listed in Table 4 as determined from a complete chemical analysis (Table 3). In addition, the amount of exchangeable lithium was determined after heating the clays to 250°C for 16 hr. According to Greene-Kelly (1955) and Schultz (1969), the less lithium fixed by heating the more beidellitic the clay; that is, the clay contains more Al in 4-fold coordination. Figure 4 shows the plot of m-equiv *p*-benzoquinone per 100 g dry clay vs the lithium exchange capacity after heating for the various montmorillonites.

#### Effects of cation fixation on the oxidizing power of a clay

The cation exchange capacities for the various clays were measured when the samples were freshly prepared and after remaining in deionized

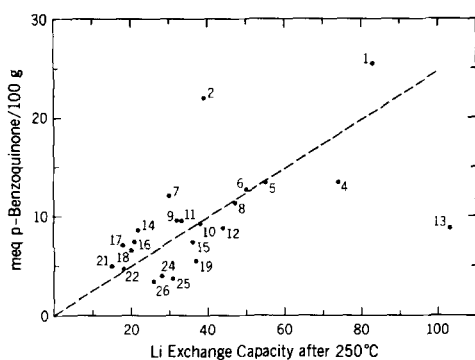


Fig. 4. Relationship between the oxidizing power of the sample (m-equiv. *p*-benzoquinone/100 g clay) and the exchangeable  $\text{Li}^+$  after heating the various samples to 250°C. The numbers correspond to those given in Table 1.

water 9 months. Table 5 gives the data for these two measurements, the Li- exchange capacities after heating to 250°C. and the cation exchange capacities after treating the 9 month old samples with tartaric acid. The effect on the oxidizing power of the clay of leaving montmorillonite in deionized water for extended periods of time is shown in Table 6. Figure 5 illustrates that the greater the ability of a clay to fix cations, the greater its ability to oxidize hydroquinone. When the cation exchange capacity of a particular clay was reduced as a result of time, the oxidizing power was also reduced.

#### Effect of reaction time

The amounts of *p*-benzoquinone formed at various reaction times for two different montmorillonites are given in Table 7. The reaction did proceed slowly, but was essentially complete after 8 hr. Thus, the data after 18 hr do reveal differ

Table 5. Cation exchange capacities

Montmorillonite	I	II	III	IV
1. K-4	98	83	27	91
2. K-4 Foundry	98	39	52	
3. Synthetic				
4. K-2	75	74	22	75
5. Gelwhite L	116	55	85	95
6. Bates Hole	98	50	71	
7. Bates Hole No. 2	98	30	92	
8. Mineral Colloid BP	120	47	96	97
9. Helms Colloid	73	32	25	91
10. Syler		38		
11. Newcastle Brown		33		
12. Volclay No. 1	102	44	67	94
13. Hectorite	104	103	95	
14. Bates Park prior 1966		22		
15. Newcastle Green		36		
16. K-2 Blue		21		
17. K-2 Good	75	18	69	
18. Bates Park 1966		20		
19. Plattenburg		37		
20. Gelwhite L No. 2				
21. Volclay No. 2		15		
22. Bates Park S. Ass.		18		
23. Bates Park Blue		30		
24. Fullers Earth		28		79
25. Bates Hole No. 1		31		
26. Volclay No. 3		26		

I—Cation exchange capacity measured within one week after saturation with Li ions.

II—Cation exchange capacity of fresh samples after heating to 250°C for 18 hr.

III—Cation exchange capacity after samples remained in deionized water for 9 months.

IV—Cation exchange capacity of 9 month old samples after treating with tartaric acid.

Table 6. Effect of aging the clays in water on *p*-benzoquinone formation

		m-equiv. <i>p</i> -Benzoquinone/100 g			
		2 weeks	3 months	6 months	1 yr
1.	K-4	46.5	33.6		
4.	K-2	24.6	20.6		
5.	Gelwhite L	24.4	21.4		9.8
6.	Bates Hole	23.2	18.3		
8.	Mineral Colloid BP	20.8	22.9	15.3	8.9
12.	Volclay No. 1	16.0	16.2		
26.	Volclay No. 3	5.4			

Table 7. Effect of reaction time on *p*-benzoquinone formation

Montmorillonite	m-equiv. <i>p</i> -Benzoquinone/100 g Dry clay		
	5 hr	18 hr	108 hr
Gelwhite L	10.6	13.4	13.9
Mineral Colloid BP	7.2	11.4	11.8

ences in oxidizing power of the clays rather than differences in reaction rates.

*Effects of oxygen, nitrogen, hydroquinone concentration, and surface area on the oxidizing power of clay*

The oxidation of hydroquinone was examined using two different starting concentrations and the results are given in Table 2. The order of oxidizing power for the various clays appears to be the same at both concentrations, but when a higher starting concentration of hydroquinone is used the amount of *p*-benzoquinone formed is higher. Table 8 gives among other results, the influence of surface area on the amount of *p*-benzoquinone formed.

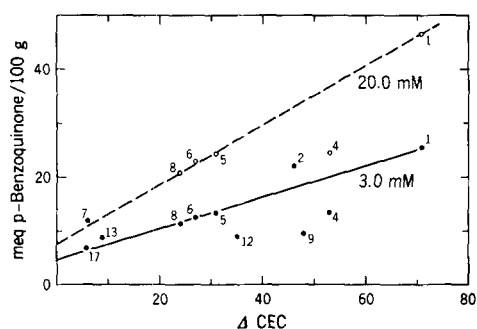


Fig. 5. Relationship between the oxidizing power of the sample (M-equiv. *p*-Benzoquinone) and the reduction in cation exchange capacity as a result of remaining in deionized water. The numbers correspond to those given in Table 1. (○) starting concentration of Hydroquinone was 20.0 mM. (●) Starting concentration of Hydroquinone was 3.0 mM.

EFFECT OF TRANSITION METAL EXCHANGEABLE CATIONS

As indicated in Table 8, the transition metal ions  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ , when in exchange sites, give rise to the oxidation of hydroquinone in both air and nitrogen. The amount of *p*-benzoquinone formed in a nitrogen atmosphere is only slightly less than that in an oxidizing atmosphere. The Fe saturated samples, after being air dried and redispersed in deionized water, showed upon determining their oxidizing power that the electron transfer properties of  $\text{Fe}^{3+}$  were greatly diminished. The reduction in oxidizing power of the iron samples was accompanied by a color change from bright yellow for the hydrated sample to brownish-orange upon drying. The samples remained brownish-orange when redispersed in deionized water. Even drying the  $\text{Cu}^{2+}$ -saturated sample at  $100^\circ\text{C}$  for 18 hr did not diminish its oxidizing power or change its color. The reflectance spectrum of the dried  $\text{Cu}^{2+}$ -saturated sample was obtained and is shown in Fig. 2 along with the reflectance spectrum of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The similarity of the two spectra indicate that the ligands were water molecules in both cases.

DISCUSSION

In most cases, hydroquinone oxidizes to form a monomeric compound, *p*-benzoquinone. Therefore, definite spectra are obtainable for both the unoxidized material and the oxidized product (see Fig. 1). In Table 2 are shown the differing amounts of *p*-benzoquinone formed by the various clays listed in Table 1. As shown by Tables 1 and 2, not only do the clays from different localities vary in reactivity, but also clays from the same mines produce varying amounts of *p*-benzoquinone, depending upon such things as prior treatment and perhaps location of the sample within the deposit. When clays are as variable as indicated above, the reactivity of the clay may be related to surface disorder rather than compositional variations.

Table 8. Effect of exchangeable cations on methylene blue determined surface area and *p*-benzoquinone formation

Montmorillonite exchangeable cation	Surface area M <sup>2</sup> /g	m-equiv. <i>p</i> -benzoquinone/100g Clay	
		Air	Nitrogen
Li-M.C.-BP	746	15.3	0.00
Na-M.C.-BP	746	15.3	0.00
K-M.C.-BP	650	12.8	0.00
Mg-M.C.-BP	290	5.9	0.00
Ca-M.C.-BP	274	8.9	0.00
Ba-M.C.-BP	150	7.0	0.00
Fe <sup>3+</sup> -M.C.-BP	368-540	24.4	(20.0)
Gel	(203-570)	(22.0)	(20.0)
Cu <sup>2+</sup> -(Gel)	(540)	(13.6)	(12.0)

#### Aluminum coordination and iron content

As mentioned earlier, Solomon *et al.* (1968) believe that the oxidation of benzidine to benzidine-blue on layer silicates arises from the interaction of the organic material with the edge aluminum and structural transition metal ions in higher oxidation states. If the coordination of aluminum and/or the reduction of ferric ions are important in oxidation reactions, then compositional differences in montmorillonites should relate to the oxidizing power.

Solomon *et al.* (1968) estimated visually the amounts of benzidine-blue generated by the various clays investigated. This method is at best qualitative. With results obtained by this method, correlation between the amount of product formed, the ferric content, and the edge aluminum (whether 4-fold or 6-fold coordination) proves to be difficult. With hydroquinone as the reactant, the amount of *p*-benzoquinone formed can be measured quantitatively (or, at the least in some cases, semiquantitatively), thereby making it possible to correlate the amount of oxidation with the total ferric iron, total aluminum, 6-fold aluminum or 4-fold aluminum.

One important compositional variable should be the amount of aluminum in 4-fold coordination; that is, the amount of beidellitic character in a smectite. Because of difficulty in obtaining complete chemical analyses for the large number of samples, a more convenient method of determining 4-fold aluminum was of value.

Table 5 presents the cation exchange capacities of Li-saturated montmorillonites after heating to 250°C. The amount of Li not fixed (presumably not captured by the octahedral layer) should be a measure of the tetrahedral aluminum (Schultz, 1969). The more Li<sup>+</sup> remaining exchangeable, the higher the tetrahedral aluminum. When *p*-benzoquinone produced is plotted against the Li remain-

ing exchangeable after heating to 250°C, a strong trend is evident (Fig. 4). In general, the greater the Li remaining exchangeable, the greater the amount of *p*-benzoquinone generated. (Point 13 is hectorite, a saponite in which the Greene-Kelly test is irrelevant. It nevertheless is plotted for information.) For the oxidizing power to be dependent upon the amount of 4-fold aluminum, the amount of tetrahedral aluminum calculated from chemical analyses should correspond to the amount of exchangeable lithium after heating at 250°C. A comparison (Table 4) of tetrahedral aluminum calculated from the chemical analyses (Table 3), to exchangeable Li after heating to 250°C, shows no relationship exists. Further, samples 1, 3, 6 and 8 (Tables 1 and 5) dried prior to Li-saturation, exhibited higher exchange capacities and greater oxidizing power than the same clays (samples 2, 16, 17, 7, 25, 14, 18, 22 and 23) which were never dried. Conversion of montmorillonite to beidellite through simple drying does not seem reasonable. Hence, lack of Li-fixation does not always establish beidellitic character and the mechanisms of this fixation probably are much more complex than proposed by Greene-Kelly (1955).

Aluminum, either 4- or 6-fold, and ferric iron are often suggested as the active oxidizing sites for organic molecules. Table 4 lists the amount of *p*-benzoquinone formed along with the Al<sup>IV</sup> and Al<sup>VI</sup> for several samples. No relationship between the oxidation and aluminum exists. Similarly, Table 4 compares the amount of *p*-benzoquinone formed and the ferric iron content; again, no relationship is demonstrated. Aluminum and iron content of a layer silicate cannot therefore always be the most crucial factors in the oxidation of organic materials by clays.

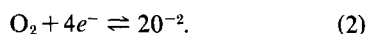
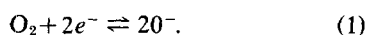
When the amounts of *p*-benzoquinone formed were plotted against the cation exchange capacities



of the heated Li-saturated samples, however, some relationship was apparent (Fig. 4). If these effects do not depend upon lattice substitutions or crystal edge phenomena, perhaps they depend upon the nature of the clay surface itself.

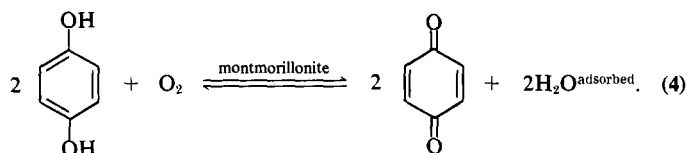
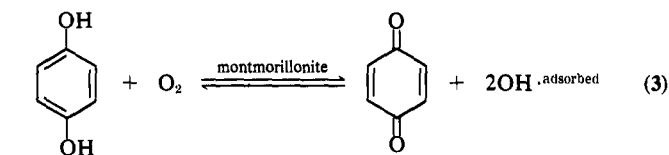
#### Nature of surface adsorbed oxygen

Possibly, the oxidation of hydroquinone and other organic materials is brought about by the activation of oxygen through chemisorption on or polarization by a clay surface. The importance of oxygen on the oxidation of hydroquinone is clearly indicated by the fact that oxidation takes place only if oxygen is available, and does not take place in the presence of a nitrogen atmosphere (Table 8) unless certain transition metal ions occupy the exchange positions. Further, the oxidizing capacity is dependent upon the source and prior treatment of the clay and not on compositional variations. These two variables should determine the surface chemistry of a montmorillonite. Khoobiar *et al.* (1968) has shown that  $\eta\text{-Al}_2\text{O}_3$  adsorbs  $\text{O}_2$  by the following mechanisms:



The predominant path was determined to involve equation 1 and only to a minor extent equation 2. This mechanism indicates that oxides are capable of bringing about the formation of oxygen radicals through chemisorption.

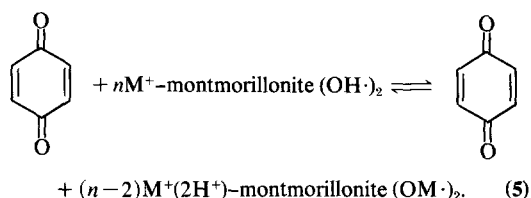
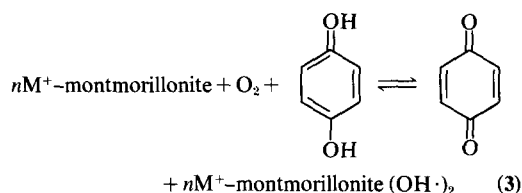
Therefore, the following mechanism is proposed for the oxidation of hydroquinone by montmorillonite:



The montmorillonite serves to a first approximation as a catalytic surface. The predominant path most likely involves equation (3). Equation (4) may be of importance for a montmorillonite in a

dry or nonaqueous state because the clay would strongly adsorb the water formed during the reaction.

The exchange cations on the clay very likely enter into the reaction. The following mechanism shows the consequence:



Equation (3) probably is the predominant path for the oxidation of hydroquinone. The symbol  $n\text{M}^+$  stands for the exchangeable cations. In equation (5) the protons which were released from the hydroquinone as a result of oxidation and combined with the oxygen radicals on the clay surface can subsequently be exchanged for the exchangeable cations on the clay. The metal ions may be held more tightly by the oxygen radical than by the exchange sites on the montmorillonite. If the above mechanism is true, the pH of the clay suspension after oxidation should be lower than the starting pH. The pH values for the various

samples were observed to be lower after oxidation had taken place, and the greatest change in pH occurred with the montmorillonite which gave the highest yield of *p*-benzoquinone.

### Effect of aging smectites in water

When the various clays were allowed to remain in deionized water for extended periods of time, the cation exchange capacities of the montmorillonite samples were reduced (Tables 5 and 6). The loss of CEC was not irreversible, but the CEC was not easily recovered unless washed with tartaric acid solution.

If the montmorillonite slurries contain oxidizable impurities (e.g. organic materials), oxygen radicals can form on the surface of the clay and the exchangeable cation can undergo the exchange reaction outlined in equation (5). If fixation of an exchangeable cation is related to the mechanism outlined in equation (5), the two following points should be observed. First, the greater the oxidizing power of the clay, the greater the number of  $O^{\cdot-1}$  radicals and the greater the reduction in cation exchange capacity. Second, a montmorillonite with a reduced cation exchange capacity should generate a reduced amount of *p*-benzoquinone. Figure 5 clearly shows that the greater the reduction in exchange capacity after nine months in deionized water, the greater the oxidizing power of the fresh clay. Five samples were examined in detail and showed that the percentage reductions in cation exchange capacity and in the amount of *p*-benzoquinone formed were equal.

### Effects of hydroquinone concentration and reaction time

Tables 2 and 7 show the effects on *p*-benzoquinone production of hydroquinone concentration and reaction time. It is not surprising that the higher the concentration of hydroquinone and/or the longer the reaction time, the higher the concentration of *p*-benzoquinone formed. Additional work is being carried out to study in detail the kinetics of these reactions.

### Effects of exchangeable cations and surface area

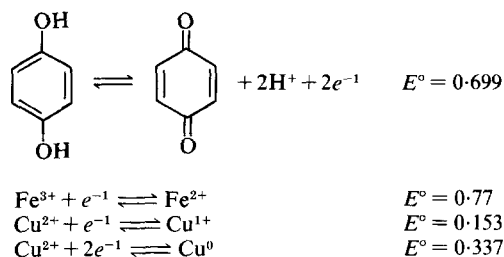
The two variables, exchangeable cations and surface area, are related because the cations saturating a montmorillonite suspended in deionized water (Brindley and Thompson, 1970) pre-determine the surface area. The Mineral Colloid BP was allowed to remain in deionized water for 6 months before the surface area measurements and oxidation experiments were carried out on the various cation saturated forms. The amount of oxidized product, in m-equiv/100 g of clay, shows a direct relationship to the methylene blue surface area when air is present (Table 8). This dependency of oxidizing power on surface area is not surprising

since the oxidation is most likely a surface activated reaction involving oxygen. The exchange cations on the montmorillonite, with the exception of  $Fe^{3+}$  and  $Cu^{2+}$ , appear to have little if any effect on the oxidizing power of a clay other than by controlling the surface area.

### Effects of transition metal ions in exchange sites

The fact that undried  $Fe^{3+}$ - and  $Cu^{2+}$ -, and dried  $Cu^{2+}$ - saturated samples were found to oxidize hydroquinone under a nitrogen atmosphere as well as in air indicates that oxygen was not required and that some exchange cations can play an active part in oxidation reactions (Table 8).

The following  $E^{\circ}$  values were given by Latimer (1964):



These  $E^{\circ}$  values are for pH = 0, even though the equilibrium pH values of the  $Fe^{3+}$  and  $Cu^{2+}$  samples were 3.0 and 4.5, respectively. At pH of 3.0 and 4.5, some  $Fe(OH)_n^{m+}$  and  $Cu(OH)_n^{m+}$  might be expected, thus influencing the  $E^{\circ}$ . The  $Cu^{2+}$  ions associated with the montmorillonite, even in the dry state, are hydrated as in  $CuSO_4 \cdot 5H_2O$ . Evidence for this statement arises from the similarity of the reflectance visible spectra of *Cu*-montmorillonite and  $CuSO_4 \cdot 5H_2O$  (Fig. 2), which indicates that  $Cu^{2+}$  ions in montmorillonite are surrounded by water molecules in a 4-fold planar symmetry. After drying, the  $Fe^{3+}$  sample, unlike the  $Cu^{2+}$  sample, was no longer reactive under a nitrogen atmosphere. Also drying caused a change in color indicating a transition from a water dispersible clay saturated with bright yellow hydrated  $Fe^{3+}$  to a nondispersible clay saturated with an orange *Fe*-hydroxy complex.

Even though the equilibrium pH values of the above samples were high enough for hydroxide formation, it appears that the montmorillonite stabilized the hydrated ions in an aqueous suspension. The clay stabilized the  $Cu^{2+}$  ion even upon drying as indicated by the visible spectrum. The  $E^{\circ}$  values for pH 0 were selected, therefore, because they represent ions which are coordinated with water molecules as ligands.

Considering the  $E^{\circ}$  of  $Fe^{3+}$ , the oxidation of

hydroquinone in an  $N_2$  atmosphere results from an electron transfer reaction involving the reduction of iron in the exchange sites. From the results of this investigation, it appears that  $Fe^{3+}$  located in the structure is not capable of being involved in oxidation or electron transfer reactions. Only when samples with easily accessible and hydrated  $Fe^{3+}$  were air dried and then redispersed did oxidation no longer take place under an  $N_2$  atmosphere. The oxidation potentials suggest that  $Cu^{2+}$  would not be involved in electron transfer reactions with hydroquinone, under an  $N_2$  atmosphere, contrary to what was observed. A possible explanation is that the layer silicate is activating either the  $Cu^{2+}$  or the hydroquinone.

Consider the following half reactions:

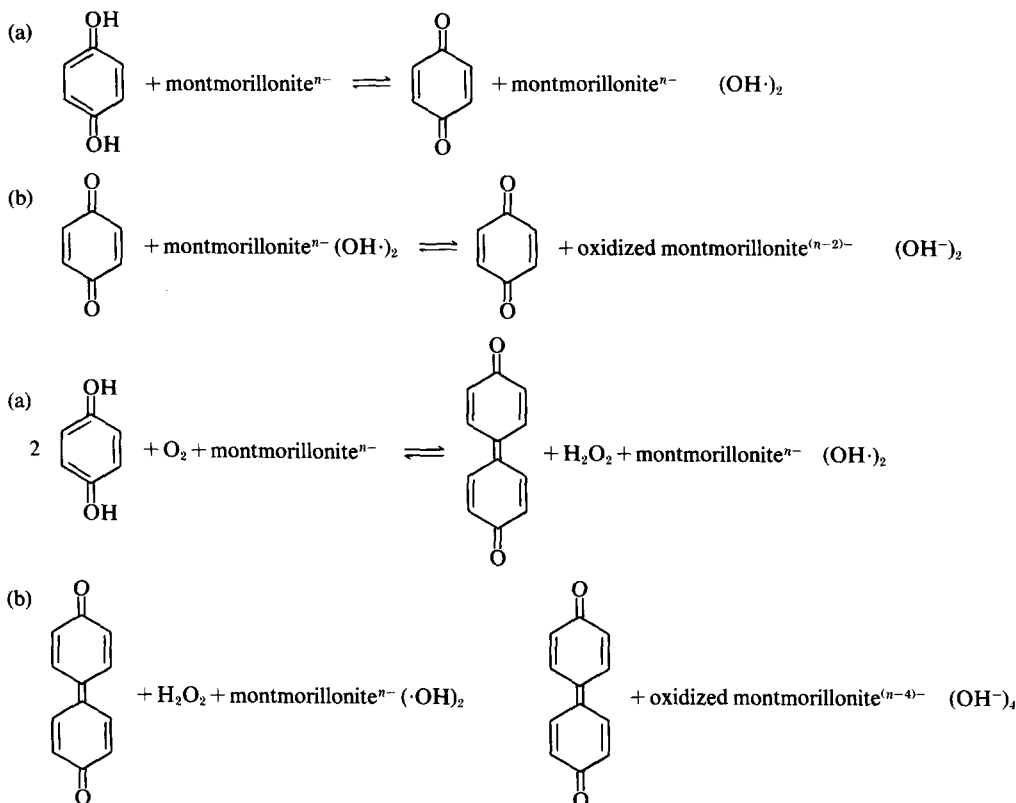
1.  $Cu^{2+} + Cl^- + e^- \rightleftharpoons CuCl$   $E^\circ = 0.54$ .
2.  $Cu^{2+} + Br^- + e^- \rightleftharpoons CuBr$   $E^\circ = 0.64$ .
3.  $Cu^{2+} + I^- + e^- \rightleftharpoons CuI$   $E^\circ = 0.86$ .

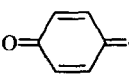
Any one of these reactions could bring about the oxidation of hydroquinone. If the montmorillonite anion behaves in a similar fashion to  $Cl^-$ ,  $Br^-$ , or  $I^-$ , the oxidation of hydroquinone could take place as a result of electron transfer involving  $Cu^{2+}$ . Montmorillonites or other clays are capable of acting as anions and, therefore, may behave in the manner

outlined above. Perhaps the montmorillonite which was saturated with  $CuCl_2$  had some  $CuCl^+$  satisfying the exchange capacity. However, the exchange capacity of the  $Cu^{2+}$  saturated clay was only slightly higher than the Na sample and the difference in the two CEC values was not high enough to account for the amount of *p*-benzoquinone formed.

#### *Effect of transition metal ions in the clay structure*

The impression that the structural iron in a montmorillonite is inert is misleading. There may be more than one mechanism by which clays participate in oxidation reactions. This possibility is borne out by the observation that blue montmorillonites, which are naturally occurring  $Fe^{2+}$ -montmorillonites, bring about the oxidation of hydroquinone and, at the same time, the oxidation of  $Fe^{2+}$  in the structure to  $Fe^{3+}$ , as indicated by the change in color from blue to yellowish-orange. No change in color occurred when samples which contained no organic material had air bubbled through them. The mechanism postulated in the previous section does not take into account the oxidation of both organic material and the structural  $Fe^{2+}$ . In order to explain the involvement of  $Fe^{2+}$ , the following two mechanisms are suggested:



The form  suggests the polymerized structure.

The net result of both mechanisms would be the formation of ferric hydroxide on the crystal edges and an oxidized organic compound. The main difference between the two mechanisms is that reaction 6 would result in the formation of a monomeric product, reaction 7 a polymeric product. One distinctive characteristic of a polymer of a polyhydric phenol is that the u.v. absorption is much broader, with an increase in optical density at about 3000 Å and less well defined than the spectrum for the pure monomeric product (Fig. 3). As mentioned earlier, most of the clay samples gave rise to *p*-benzoquinone with little if any broadening of the absorption band. Further, in the Li-saturated Mineral Colloid BP sample, polymerization was absent because the amount of hydroquinone remaining after oxidation corresponded to the difference between the amount originally present and the amount of *p*-benzoquinone formed. In the case of the two blue montmorillonites, the absorption band at 2460 Å was broader with a definite increase in optical density at 3200 Å than was the case for the other clay samples, thus indicating that some polymerization of *p*-benzoquinone had occurred. Therefore, the second mechanism is predominant when a reduced montmorillonite or a montmorillonite containing Fe<sup>2+</sup> is involved in oxidation.

#### *Sampling and processing implications*

Clays with the same chemical composition and from the same deposit (or geographic area) have been examined and found to differ greatly in oxidizing power. Samples 8, 14, 18 and 22 are of similar composition, but, as shown in Table 2, vary greatly in oxidizing power. The same behavior was shown by samples 1 and 2, 4 and 17, 5 and 9, and 6, 7 and 25 when comparisons are made within each group. Only the first group (8, 14, 18 and 22) will be discussed in detail. The same observations will apply to the other groups.

Sample 14, Bates Park prior to 1966, was the source of material for sample 8, Mineral Colloid BP. Calgon, 0.25 per cent by weight was added to the crude clay to disperse it prior to commercial fractionation to remove the coarser non-clay material. The product was then dried and ground. Thus, the Mineral Colloid BP had been dried and pulverized before lithium saturation and fractionation.

The other samples, 14, 18 and 22 were collected

in the field (Table 1) and neither dried nor pulverized prior to Li saturation and fractionation. The principal difference between samples 8 and 14 is primarily that sample 8 was dried and pulverized and sample 14 was never allowed to dry. Cations of amorphous material blocking active oxidation sites on the clay may have been made exchangeable by the drying and grinding. Such cations would then be removed during the lithium saturation procedure, causing an increase in the oxidizing power of the montmorillonite. The Calgon treatment has little if any effect because the same trend is observed for the K-4 and K-2 samples. In both of these cases, neither the dried and pulverized nor undried samples had been treated with Calgon. The less reactive samples were found to be those which were never dried prior to saturation with Li ions.

If the amount of Fe<sup>3+</sup> at crystal edges could explain the observed differences in clays from the same deposit or the differences between dried and undried samples, one would expect blue montmorillonite to produce less *p*-benzoquinone than the yellow form. Samples 16 and 17, which are the unoxidized and oxidized varieties of K-2, show just the opposite behavior, thus indicating the differences in oxidizing power between geologically related samples cannot be explained by Fe<sup>3+</sup> content. Incidentally, for sample 16 and to a greater extent for sample 23, the amount of oxidation may be greater than indicated in Table 2 because of the increase in background and broadening of the absorption band due to formation of a polymeric compound.

Major differences in surface properties clays coming from the same geological location can result from differences in treatment of the samples, as well as from mineralogical, geological, or chemical variations. Therefore, when comparing clays from the same geological location, it is important that the treatment of the samples be identical.

#### SUMMARY AND CONCLUSIONS

This investigation has demonstrated the importance of (the chemisorption or polarization of) oxygen in determining the reactivity of a layer silicate in oxidation reactions run under aqueous conditions. Additionally, the past history of a clay, including the steps used in its purification and subsequent handling, affects the reactivity of a montmorillonite. The secondary factors are the exchangeable cations, surface area, concentration of organic material and length of reaction time.

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**Résumé**—Le pouvoir oxydant d'une smectite peut être mesuré quantitativement par oxydation de l'hydroquinone en *p*-benzoquinone dans une pâte d'argile. L'oxydation a lieu en présence de  $O_2$  (air) mais pas en présence de  $N_2$  à moins que  $Fe^{3+}$  et  $Cu^{2+}$  ne soient les cations échangeables. Cette étude a porté sur 26 échantillons de smectite de compositions différentes et ayant subi des traitements variés. Le pouvoir oxydant augmente lorsque la fixation de Li décroît et lorsque la capacité d'échange cationique augmente. La fixation de Li ne dépend pas de Al tétraédrique. La capacité d'échange cationique peut diminuer notablement à la suite d'une simple conservation dans l'eau.

L'oxydation a lieu principalement sur la surface, par le biais des molécules d'oxygène ou des radicaux adsorbés. Un mécanisme est proposé. En présence de  $Fe^{3+}$  ou  $Cu^{2+}$ , même sans  $N_2$ , l'oxydation existe par suite de transferts d'électrons. Dans le cas des smectites contenant  $Fe^{2+}$ , Fe et l'hydroquinone sont oxydés simultanément au cours de la même réaction.

**Kurzreferat**—Die Oxidationskraft eines Smectits kann durch Oxidation von Hydrochinon zu *p*-Benzochinon in einer Tonaufschlammung quantitativ gemessen werden. Die Oxidation findet in Gegenwart von  $O_2$  (Luft), aber nicht von  $N_2$  statt, außer, wenn  $Fe^{3+}$  oder  $Cu^{2+}$  die austauschbaren Kationen sind. In dieser Untersuchung wurden 26 Smectitproben unterschiedlicher Zusammensetzung und Vorbehandlung untersucht. Die Oxidationskraft steigt mit abnehmender Li-Fixierung und zunehmender Kationenaustauschkapazität an. Die Li-Fixierung hängt nicht vom Gehalt an tetraedrischem Al ab. Die Kationenaustauschkapazität kann allein durch Aufbewahrung in Wasser erheblich herabgesetzt werden.

Die Oxidation verläuft grundsätzlich an der Oberfläche durch absorbierte Sauerstoffmoleküle oder Radikale. Ein Mechanismus wird vorgeschlagen. In Gegenwart von  $Fe^{3+}$  oder  $Cu^{2+}$  tritt, sogar unter

$N_2$ , Oxidation durch Elektronenübergang ein. An Smectiten, die  $Fe^{2+}$  enthalten, werden sowohl das Eisen als auch das Hydrochinon in derselben Reaktion oxidiert.

**Резюме** — Окислительную активность смектита можно количественно измерить посредством окисления гидрохинона в шламме глины с выходом р-бензохинона. Окисление происходит в присутствии  $O_2$  (воздух), но в присутствии  $N_2$  только тогда, когда  $Fe^{3+}$  или  $Cu^{2+}$  являются обменными катионами. В этой работе исследовалось 26 образцов смектита в различных смесях и различными методами переработки. С понижением Li-фиксации и с повышением способности катионообмена интенсивность окисления повышается. Li-фиксация не зависит от тетраэдрального Al. Простое хранение в воде может заметно понизить способность катионообмена.

Окисление происходит главным образом на поверхности вследствие адсорбированных молекул или радикалов кислорода. Предполагают, что в присутствии  $Fe^{3+}$  или  $Cu^{2+}$ , даже в присутствии  $N_2$ , окисление происходит через перенос электронов. Если смектиты содержат  $Fe^{2+}$ , то и Fe и гидрохинон окисляются одновременно.