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ACTIVATION OF CLAYS.

PART ONE

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D.C. Lawrie.

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ACTIVATION OF CLAYS.

PART ONE

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ACTIVATION OF CLAYS.

PART ONE

Abstract.

1. Cation exchange capacities of some local clays have been determined by a method which measures the adsorption of methylene blue. It is shown that the method is not altogether satisfactory.

2. Acid leaching experiments on three local clays and one New Zealand clay are described. It is shown that two of the local clays can be made highly active in decolourizing dirty oil. Conditions for maximum activation by acid leaching are roughly evaluated.

1. INTRODUCTION.

The activity of certain clays in bleaching and other adsorptive processes has long been known and used in industry. The evaluation of individual clays for such purposes is entirely empirical. A great deal of research on activity and activation of clays has been carried out since 1930, but as yet, the factors underlying activity remain obscure.

Many different clays have proved useful as oil decolourizing agents, although quite often it is found that of two clays which appear structurally and chemically the same, one may decolourize oil to a high degree while the other is of little use in this respect.

Clays of the montmorillonite group are usually associated with a high degree of activity. Clays of this type have a relatively large number of exchangeable cations, and high exchange capacity has been associated with decolourizing activity. However, no general relationship has been found between exchange capacity and activity. Although active clays usually have relatively high capacities, not all clays of high capacity are active.

Some naturally active clays have been improved by acid leaching. In fact some of the best decolourizing clays are prepared from certain bentonites of relatively low natural decolourizing ability.

In the broader scope of this project it is hoped to throw some light on the reasons for natural clay activity, and the factors involved in the improvement of activity by acid leaching. However, the initial work has been confined to a more or less empirical study of a few local clays, some of which have proved activable to a possibly commercial degree. The evaluation of these clays is incidental to the longer term project. It is hoped that the data obtained from leaching studies may eventually prove useful in forming an explanation of improved activity.

2. MATERIALS EXAMINED.

The following clays have been used in the investigation. Each is identified by a letter:

A. From Hackham railway cutting.
B. " " " "
C. " Halletts Cove.
D. " Port Willunga.
E. " Hackham railway cutting.
F. " " " "
G. " " " "
H. " Noarlunga.
J. " New Zealand.
K. Imported Fullers Earth, ex Shell Co.
L. From Birdwood (Kaolin deposit).
M. " Lake Fowler, Yorke Peninsula.

Another imported Fullers Earth sample, designated 500 C, has also been used.

All local clays were elutriated to eliminate sands, dried, and ground to pass 200 mesh.

Only samples C, F, J, and M have been used in leaching tests to date.

3. ANCILLARY MATERIALS.

The "dirty oil" used for decolourizing tests was obtained from The Shell Oil Co. reclamation works at Birkenhead. This is used crankcase oil which has been steam and acid treated, neutralized with lime, and filtered. Thus it is in the condition immediately prior to the final clay-treatment stage.

4. EXPERIMENTAL PROCEDURE AND RESULTS.

4.1 Determination of Cation Exchange Capacities of Clays.

Exchangeable cations have been determined in most of the clays listed by a method due to Robertson and Ward (1). The method is to measure the adsorption of methylene blue by the clay, the authors claiming that under prescribed conditions, this adsorption is almost entirely by cation exchange.

Method.

A suitable weight of clay is transferred to a glass-stoppered bottle, and 25 ml. of standard methylene blue solution (approximately 0.3%) added by pipette. The mixture is shaken for 20 minutes and then centrifuged. An aliquot of the supernatant liquor is suitable diluted in 0.1 N acetic acid, and the optical density measured at a wavelength of 620 milli-microns, against a reference of distilled water. Using a standard optical density curve for methylene blue, the amount of dye adsorbed on the clay can be determined, and hence the cation exchange capacity calculated.

The dry weight of clay required for this test is that which, after adsorption under the specified conditions, leaves in solution between 0.5 and 15 per cent of the original dye.

Two or three tests are usually required to determine the amount of clay required to satisfy this condition. The preparation and standardization of methylene blue solutions is described in an appendix to this report. The exchange values determined for the various clays are shown in Table 1.

The exchange capacity of Fullers Earth 500C was also determined on duplicate samples by conversion to the calcium form, eluting and estimating the calcium.

Procedure.

The clay samples, in small Buchner funnels, were first washed with ammonium nitrate solution to eliminate any free sulphate, then with approximately 30 volumes of normal calcium nitrate solution. Gentle suction was used to give a very slow liquor transfer. The clays were then washed with 95 per cent ethyl alcohol, and eluted with 2 normal ammonium chloride solution. Calcium was determined in the eluates by precipitation as oxalate, igniting the precipitate and weighing the oxide. The exchange capacity values determined for the clay are also shown in Table 1.

TABLE 1.

Cation Exchange Capacities.

Clay	Capacity meq/100 g.
Methylene blue adsorption method.	
A (Hackham)	39.5
B (")	35.5
C (Halletts Cove)	29
D (Pt. Willunga)	21
E (Hackham)	40
F (")	41
G (")	40
H (Noarlunga)	17
J (New Zealand)	11
L (Birdwood)	2
Fullers Earth 500C	55
Calcium elution method.	
Fullers Earth 500C: (1)	73.2
Fullers Earth 500C: (2)	72.8

4.2 Acid Activation of Clays.

Note: All acid treatments are identified by the letter designating the raw clay, followed by a stroke, then a number in the sequence 1, 2, 3, etc. for succeeding leaches of each clay.

4.2.1. Standard Leaching Procedure.

15 g. (dry weight) of clay is refluxed with sulphuric acid of varying concentration at a pulp density of 30 per cent solids, for varying periods of time. In some cases, sodium chloride is added to the leach.

Leaching is carried out in 100 ml. Quickfit flasks fitted with two-way adaptors. Mechanical stirring is provided through a special sealed ball-race carried centrally in the adaptor, and a water-cooled condenser is fitted to the other (side) arm of the adaptor. An electric hot plate is used for heating. At the end of the leach period, the clay is filtered on a small Buchner funnel, and washed with distilled water. The filtrate and washings are made up to a volume of 100 ml. for analysis. The filtered clay is further washed, air-dried, and ground to pass 200 mesh.

4.2.2. Hackham Clay.

In the first leach, F/1, 60 g. dry weight of clay were mixed with 100 ml. of distilled water in a 250 ml. flask. 47 g. of concentrated hydrochloric acid were added, and the mixture heated by a mantle heater. Mechanical stirring was provided through a short air condenser in the neck of the flask.

The clay was refluxed for 2 hours, then filtered and washed on a Buchner funnel. The filtrate and washings were made up to 250 ml. and the liquor was analysed for alumina, iron, calcium, and free acid. The clay was further washed with distilled water, air dried, and ground to pass 200 mesh.

Subsequent leaches of clay F were carried out according to the Standard Leaching Procedure.

Details of acid strength, leach time, and sodium chloride added, for leaches of Hackam clay:

TABLE 2.

Leaches of Hackham Clay.

Leach No.	Leach time hr.	Acid strength % w/v	NaCl added g.
F/2	$5\frac{1}{2}$	25	–
F/3	$5\frac{1}{2}$	10	4
F/4	$5\frac{1}{2}$	10	–
F/5	$5\frac{1}{2}$	20	–
F/6	$5\frac{1}{2}$	30	–
F/7	8	25	–

The leach liquors were analysed for alumina, iron, and free acid. Analytical results are shown in Table 3.

TABLE 3.

Leach Liquor Analyses.

Liquor	Vol. ml.	Al_2O_3 g/l	Fe_2O_3 g/l	Free acid (H_2SO_4) g/l	CaO g/l
F/1	250	9.4	14.0	14.2[a]	2.5
F/2	100	7.2	11.2	15.8	–
† F/3	"	0.9	5.9	8.7	–
F/4	"	2.3	3.04	8.4	–
F/5	"	6.7	7.38	14.8	–
F/6	"	11.0	11.96	15.8	–
F/7	"	9.7	7.08	16.1	–

a. Hydrochloric acid. † NaCl added to leach.

4.2.3. Halletts Cove Clay.

The standard procedure was followed for leaches of this clay, except that in leaches C/1, C/2 and C/3, the flasks were fitted with short air condensers, and the stirrers operated through them. Details of acid strength, time, and sodium chloride added for the particular leaches are shown in Table 4.

TABLE 4.

Leaches of Halletts Cove Clay.

Leach No.	Leach Time hr.	Acid Strength % w/v	NaCl added g.
C/1	5½	10	-
C/2	5½	15	-
C/3	5½	20	-
C/4	10	15	-
C/5	10	20	-
C/6	10	25	-
C/7	5½	20	8
C/8	8	20	-

As before, leach liquors were analysed for alumina, iron, and free acid, and the results are shown in Table 5.

TABLE 5.

Leach Liquor Analyses.

Liquor	Vol. ml.	Al_2O_3 g/1	Fe_2O_3 g/1	Free Acid (H_2SO_4) g/1
C/1	100	1.35	4.84	11.1
C/2	"	2.55	8.14	14.7
C/3	"	3.0	13.23	16.2
C/4	"	6.8	1.93	8.4
C/5	"	11.5	2.80	11.1
C/6	"	13.6	3.13	11.1
† C/7	"	9.2	8.28	9.4
C/8	"	11.8	2.39	11.3

† NaCl added to leach.

4.2.4. New Zealand Clay.

Three leaches of this clay were carried out, each at a pulp density of 30% solids. In each case a 30 g. sample of dry clay was leached under reflux for 5½ hours with 70 g. of sulphuric acid solution. The acid strengths used in the respective leaches J/1, J/2 and J/3 were 10%, 15% and 20% (w/v). Leach pulps were stirred mechanically through short air condensers, whilst heated on an electric hot plate.

At the end of the leaching period, the clays were filtered on Buchner funnels and washed. The filtrates and washings, were made up to 200 ml. and the liquors analysed for alumina, iron and free acid. The results are shown in Table 6. The clays were further washed, air-dried, and ground to pass 200 mesh.

TABLE 6.

Leach Liquor Analyses

Liquor	Vol. ml.	Al_2O_3 g/1	Fe_2O_3 g/1	Free Acid (H_2SO_4) g/1
J/1	200	10.0	0.55	0.95
J/2	"	12.7	0.86	3.2
J/3	"	18.0	1.51.	2.6

4.2.5. Lake Fowler Clay.

The standard procedure was followed for all leaches of this clay. Particulars of individual leaches are shown in Table 7. No sodium chloride was added to these leaches.

TABLE 7.

Leaches of Clay M.

Leach No.	Leach time hr.	Acid Strength % w/v
M/1	6	15
M/2	6	20
M/3	6	25
M/4	6	30
M/5	4	25
M/6	4	30
M/7	6	5

The leach liquors were analysed for alumina, iron, and free acid, and the results are shown in Table 8.

TABLE 8.

Leach Liquor Analyses.

Liquor	Vol. ml.	Al_2O_3 g/l	Fe_2O_3 g/l	Free Acid (H_2SO_4) g/l.
M/1	100	4.8	3.0	24.9
M/2	"	6.6	4.5	31.3
M/3	"	8.0	6.1	41.0
M/4	"	10.3	7.6	45.0
M/5	"	8.0	6.0	41.8
M/6	"	10.3	6.95	48.8
M/7	"	1.4	1.19	7.5

4.3 Oil Decolourizing.

The standard procedure for determining the oil-decolourizing power of a clay is as follows.

20 ml. of dirty oil in a 50 ml. beaker is mechanically stirred and heated on an electric hot plate. When the oil temperature reaches 40°C, 2 g. (dry weight) of clay is added and thoroughly mixed in. The mixture is heated at a rate which brings the temperature to 150°C in 10 minutes, and this temperature is maintained for a further 10 minutes. The oil is then filtered through a Whatman No. 42 paper on a very small Buchner funnel, and collected in a dry 100 ml. flask. The funnel is kept heated with a heating tape during filtration. 10 ml. of the filtered oil is diluted to 50 ml. with light kerosene, and the optical transmission measured in ½ inch tubes at a wavelength of 430 millimicrons. The standard for reference is the diluted oil obtained by treating the dirty oil with the imported Fullers Earth, K, according to the above scheme.

Each of the acid treated clays derived from the leaching experiments, and the corresponding raw clays, has been tested in this manner. The relative light transmissions of the resulting oils are shown in Table 9.

TABLE 9.

Oil Decolourizing Ability.

Clay		% Light Transmission of Treated Oil.
F	(Hackham)	41
F/1	"	87
F/2	"	97
⌿ F/3	"	71
F/4	"	67.5
F/5	"	92
F/6	"	99
F/7	"	95
C	(Halletts Cove)	50
C/1	"	70
C/2	"	75
C/3	"	82
C/4	"	82
C/5	"	79
C/6	"	74
⌿ C/7	"	84
C/8	"	78
J	(New Zealand)	45
J/1	"	61
J/2	"	67
J/3	"	85
M	(Lake Fowler)	25
M/1	"	43
M/2	"	45
M/3	"	44
M/4	"	41
M/5	"	47
M/6	"	44
M/7	"	30

⌿ NaCl added to leach.

5. DISCUSSION.

5.1 Cation Exchange Capacity.

The methylene blue method for determining cation exchange capacity is stated to give generally lower results than the more usual methods of eluting and determining a particular ion (1). However, Robertson and Ward claim that this method gives a real measure of cation exchange capacity, and advance reasons which they believe could explain why determination of barium eluted from a clay may give a high value.

The duplicate results obtained for the Fullers Earth 5000 by determination of exchanged calcium are in very close agreement, and it is felt that the explanations advanced by Robertson and Ward for a high result may not be valid. They suggest precipitation of additional barium in the clay by free carbonate and sulphate. Free sulphate and carbonate in the above samples should have been replaced in the preliminary wash with ammonium nitrate solution. It is difficult to see why the values determined by the calcium method should not be reasonably true. The methylene blue method gives a value for Fullers Earth 5000 which is 25 per cent lower than that obtained by the calcium method and it would therefore seem that the methylene blue method is open to some doubt. However, the method is probably a reliable enough indication of the capacity of a clay.

The low results obtained by the methylene blue method may be explained by the insistence on the condition of adsorbing 85 per cent of the dye present. The resulting exchange equilibrium may thus be somewhat short of complete saturation of the clay exchange sites with methylene blue cations.

At this stage, work on exchange capacities was discontinued, because from the results obtained, and from the literature, it appears there is no correlation between exchange capacity and decolourizing activity in clays. If there is any connection between the two, then it is confounded by other factors.

5.2 Acid Leaching of Clays.

5.2.1. General Discussion.

From the leaching experiments on the various clays, and oil decolourizing tests of the products, it appears that the clay activity is related in a significant manner to the amount of alumina removed by leaching. The clay activity increases to a certain value, and decreases as this value is exceeded. The amount of alumina removed at maximum activity varies from one clay to another. Figure 1 shows graphs of treated oil transparency plotted against alumina removed from the treated clays.

It is not practicable to make further discussion of these results at the moment, as reports on petrographic and X-ray diffraction examination of the clays are not yet available. These reports and further data will be required before any interpretation can be made.

5.2.2. Effect of Addition of Sodium Chloride to Leaches.

Sodium chloride was added to leaches F/3 and C/7. The comparable leaches without sodium chloride added are F/4 and C/3 respectively. Although the products obtained from the chloride leaches in each case yielded an oil of slightly better light transmission than the clays leached without chloride, the difference was very small. However, the clays leached with added chloride appear to yield a significantly lighter oil than would be expected for the amount of alumina removed. The points corresponding to clays F/3 and C/7 in the graphs of treated oil transparency against alumina removed (Fig. 1) are marked with circles, and it is evident that these points are anomalous, and well above the curve obtained from clays leached without chloride.

5.2.3. Hackham Clay, F.

The data show this clay to be a likely commercial proposition for decolourizing used crankcase oil. It can be made almost as active as the imported Fullers Earth at present used by the Shell Oil Company. Acid required for suitable treatment would probably amount to 850lb. of sulphuric acid per short ton of raw clay.

5.2.4. Halletts Cove Clay, C.

This clay also appears to be activable to a possibly commercial degree. Acid requirements would probably be of the order of 650 lbs. of sulphuric acid per short ton of raw clay.

5.2.5. New Zealand Clay, J.

This clay is reported as already being commercially treated. Very little has been done with this clay since some local clays appeared appreciably activable. It was included in the investigation only because it is a known activable clay. Since others were discovered, there was no point in persisting with this sample.

The leaches carried out do not appear to have activated the clay to its maximum, as seen from the curve in Figure 1.

5.2.6. Lake Fowler Clay, M.

The leaches carried out on this clay have shown that it is not sufficiently activated by this type of treatment to achieve commercial interest. It was observed that for leaches of 4 hours and 6 hours duration respectively with 25 per cent and 30 per cent acid, the clay derived from the shorter leaching term was slightly superior in each case, although the amount of alumina removed at each acid strength was constant for both periods of leaching.

6. REFERENCES.

(1) Robertson and Ward: "The Assay of Pharmaceutical Clays", J. of Pharmacy and Pharmacology, Vol. 3, 1951.

APPENDIX.

1. Determination of Moisture in Clays.

The moisture content had to be known for all raw and acid treated clays. This was determined by drying the clays overnight (16 hr.) in an oven at 105°C.

2. Preparation and Standardization of Methylene Blue Solution.

3.0 g. of BDH standard stain methylene blue (hydrochloride) was dissolved in hot distilled water, cooled, and made up to one litre in a volumetric flask.

This solution was standardized by precipitation of the dye dichromate by addition of a measured volume of standard potassium dichromate solution. The excess dichromate was titrated with standard ferrous ammonium sulphate solution.

The standard dye solution contained 0.261 per cent of methylene blue.

3. Optical Absorption Spectrum of Methylene Blue Solution.

A sample of the standard dye solution at a dilution of 1:500 was used to obtain an absorbance curve. The transmittance of this solution was measured over the range 400 to 700millimicrons, using distilled water as a reference.

Maximum absorbance occurred at 620 millimicrons.

4. Standard Curve for Optical Estimation of Methylene Blue Solutions.

Aliquots of the standard dye solution were diluted in 0.1 normal acetic acid by factors of 1000 up to 10000. Optical densities of the resulting methylene blue solutions were measured at a wavelength of 620 millimicrons, against distilled water as reference. The dye concentrations expressed as parts per million were plotted against optical density to give a standard curve, which was linear over the concentration range given.

Note: Acetic acid was used in dilutions of the dye solution to inhibit adsorption of the dye on glass-ware.

5. Optical Transmittance of Reclaimed Oil.

A sample of reclaimed oil (Shell Oil Co. Ltd.) diluted with light kerosene to five times its volume was used to obtain an absorbance curve. The per cent transmittance was measured over a range of wavelengths from 400 to 700 millimicrons, using distilled water as a reference.

A maximum absorbance peak occurs at a wavelength of 430 millimicrons. This wavelength was used for comparison of variously bleached oil samples.

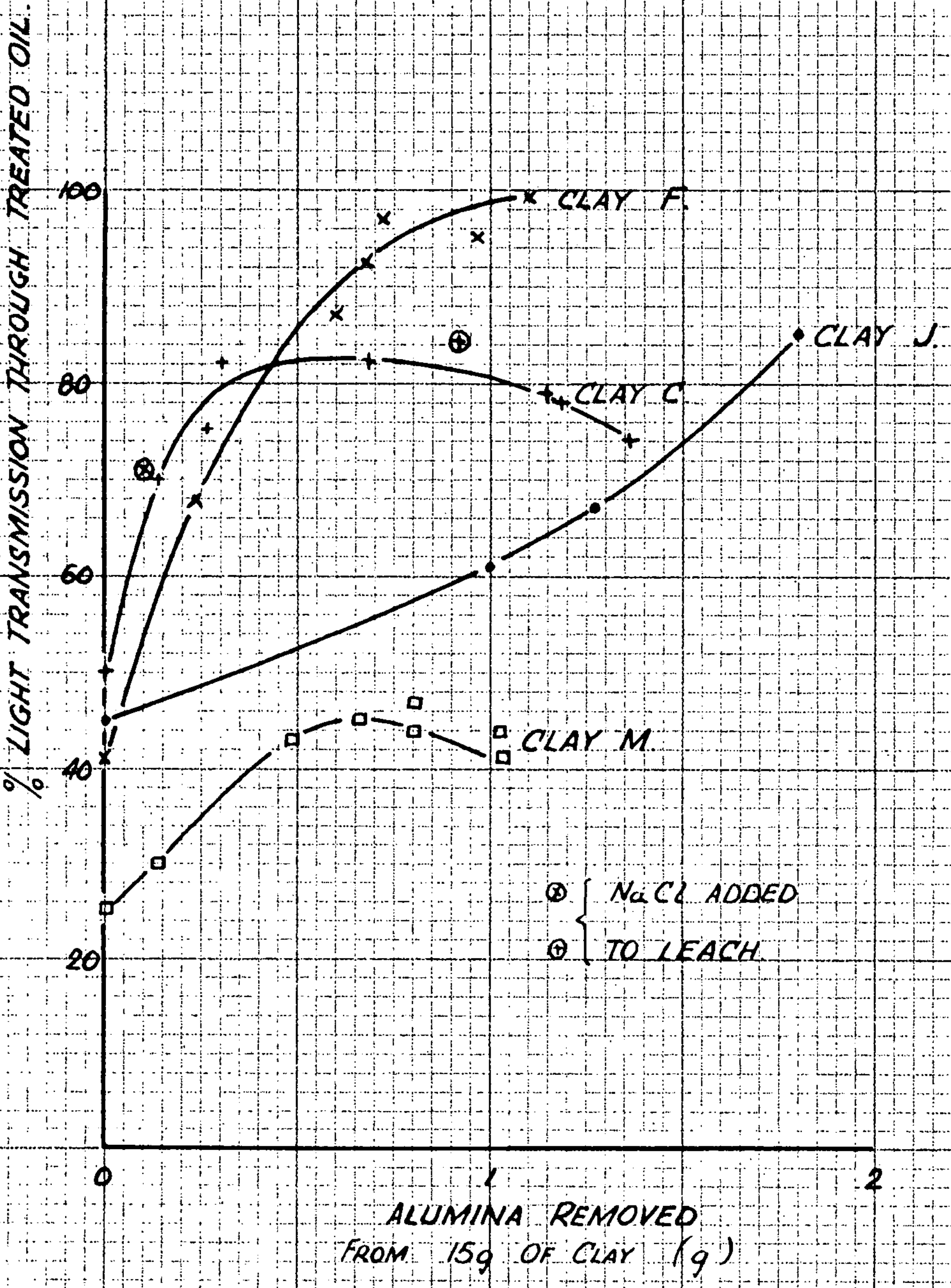

FIGURE-1

OIL DECOLOURIZING WITH ACID LEACHED CLAY

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