PROVINCE OF SASKATCHEWAN

DEPARTMENT OF MINERAL RESOURCES

HON. J. H. BROCKELBANK, MINISTER C. A. L. HOGG, DEPUTY MINISTER

Acid Activation of Saskatchewan Bentonites

by

A. A. Winer

Industrial Minerals Research Branch
R. V. Tomkins, Director
1954

PRICE: $1.00

REPORT OF INVESTIGATIONS
No. 4

CONTENTS

Page

TABLES

FIGURES

BENTONITE

Bentonite is composed mainly of montmorillonite, a clay mineral which was formed in most instances by the alteration of volcanic dust laid down in waters of earlier eras. The montmorillonite minerals have been described and their properties set forth by Ross and Hendricks (16) of the United States Geological Survey. The major features of the crystal structure are three-layer plates consisting of a layer of silicon in tetrahedral co-ordination on either side of a single layer of aluminum in octahedral co-ordination with oxygen and hydroxyl in the anion positions. This, in the unsubstituted form, is pyrophyllite (Fig.1). In montmorillonite, divalent magnesium is substituted for some of the trivalent aluminum in octahedral co-ordination resulting in negative charges on the three-layer sheet. These are balanced by adsorbed cations between the plates, usually sodium or calcium. Ferric iron often substitutes for aluminum also, but as it is trivalent, there is no unsatisfied charge. The interlayer ions are determined partially by the original geochemical environment. As these cations are exchangeable, they may be determined to some extent by subsequent history. Base exchange may also be attributed to the OH-Si-Al linkage developed on lateral broken surfaces.

Water is also adsorbed between the plates. The important characteristics of sodium bentonite are due mainly to this property. Calcium bentonite also adsorbs water but to a lesser degree. Grim, in his recent book (9, pages 161-189) has reviewed the theories for the mechanism by which the water is held. There is general agreement that adsorbed sodium ions cause the water molecules to assume some type of orientation for a considerable distance from the clay particle. This water loses its liquid character as in a hydrate, and consequently high viscosity suspensions can be developed with a low concentration of sodium montmorillonite. When calcium is the adsorbed ion, the orientation of water molecules ceases much closer to the particle.

The adsorbent quality of bentonite also depends upon the extent and quality of the surface developed by action of weathering agents. This quality unfortunately has no accurate means of measurement at present and samples must be compared to a standard clay.

A chemical formula of calcium montmorillonite, after Ross and Hendricks (9) would be

$$(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2\left(\frac{Ca}{2}\right)_{0.33}$$

Where $Al_{1.67}Mg_{0.33}$ represents ions with octahedral co-ordination

Si_4O_{10} represents ions with tetrahedral co-ordination

$O_{10}(OH)_2$ represents oxygen and hydroxyl

$\left(\frac{Ca}{2}\right)_{0.33}$ Represents exchangeable calcium

USES, SOURCES, AND PRODUCTION

The non-swelling bentonite used as a source for decolorizing agents and cracking catalyst comes mainly from southern United States. The greatest consumption of the material is as a decolorizing clay, but its use as a cracking catalyst is becoming increasingly important in both the United States and Canada. There are some minor uses such as foundry sand bond, which account for a small proportion of the total bentonite of this type consumed.

Sodium or swelling bentonite is used mainly as a drilling 'mud' in oil well drilling, but a considerable tonnage is also used as a foundry sand bond. Sodium bentonite for the above uses is produced almost entirely from western South Dakota and eastern Wyoming.

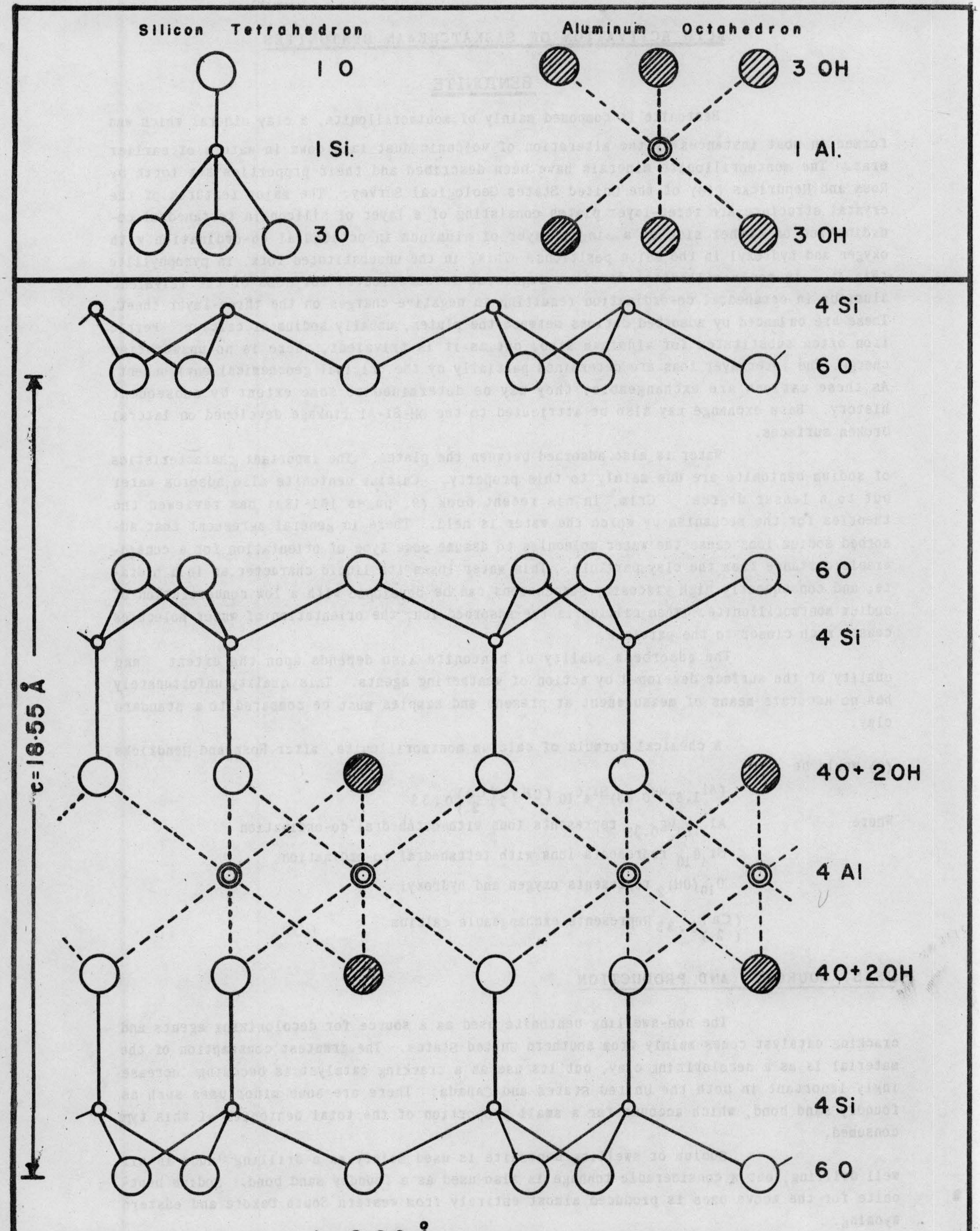


FIGURE I. PYROPHYLLITE STRUCTURE.

In 1952, 50 percent of all bentonite produced in the United States was used in rotary-drilling mud, 23 percent for foundry-sand bond, 21 percent for filtering and decolorizing oils, and 6 percent for a variety of other uses, according to the United States Bureau of Mines (20). In that year a record production of 1,412,902 tons was reached, which was an increase of 17 percent over 1951,although all other clay mineral production decreased, Mainly responsible for this increase was a 53 percent rise in the quantity of bentonite used for rotary-drilling gel.

Canadian production of bentonite is limited to a few hundred tons of of drilling mud in Alberta, and from 10,000 to 15,000 tons of activated bentonite in Manitoba, the latter material being shipped to oil refineries in Eastern Canada. Canadian consumption was 32,694 tons in 1952 according to the Dominion Bureau of Statistics. A little more than half, 17,000 tons, was drilling mud, used in Western Canadian oil exploration: 21 percent was consumed by iron and steel foundries: 22 percent was used for refining petroleum and vegetable oils.

BENTONITE IN SASKATCHEWAN

Occurrences of bentonite in Western Canada were described by Ries and Kiele (15), Ells (6), Spence (18), and other officers of the Dominion Department of Mines in the early part of the century. Worcester (22) has explored and carried out tests on deposits of bentonite during the past 30 years.

Bentonite occurs in the Vermilion River formation (upper Cretaceous) in the northeast part of Saskatchewan, the largest known deposit being on the Swan River north of Pelly. This is the calcium bentonite which was used in the detailed investigation described in this report. Similar bentonite occurs in the Riding Mountain formation (later Upper Cretaceous) which underlies a large area in the eastern part of the province. Small deposits have been located south of Moosomin, but none of commercial size. However,this formation is of regional extent and has not been prospected in any detail. There is a good chance that further exploration will disclose commercial tonnages. Other 'non-swelling' bentonite is found west of Rock Glen and is of Tertiary age occurring in the Ravenscrag formation. A large deposit of semi-bentonite occurs near Knollys in the Frenchman river valley in the Southwest, and other showings are found in this area in the Battle formation, at the top of the Upper Cretaceous.

The bentonites which exhibit swelling characteristics are found in an area extending from the west end of Twelve Mile Lake to St. Victor and farther to the southeast in the Big Muddy valley. These deposits are found in the Ravenscrag formation. Two of the larger exposures are found at Pickthall siding and just north of St. Victor.

Locations of these deposits are shown on the accompanying map, Figure 2.

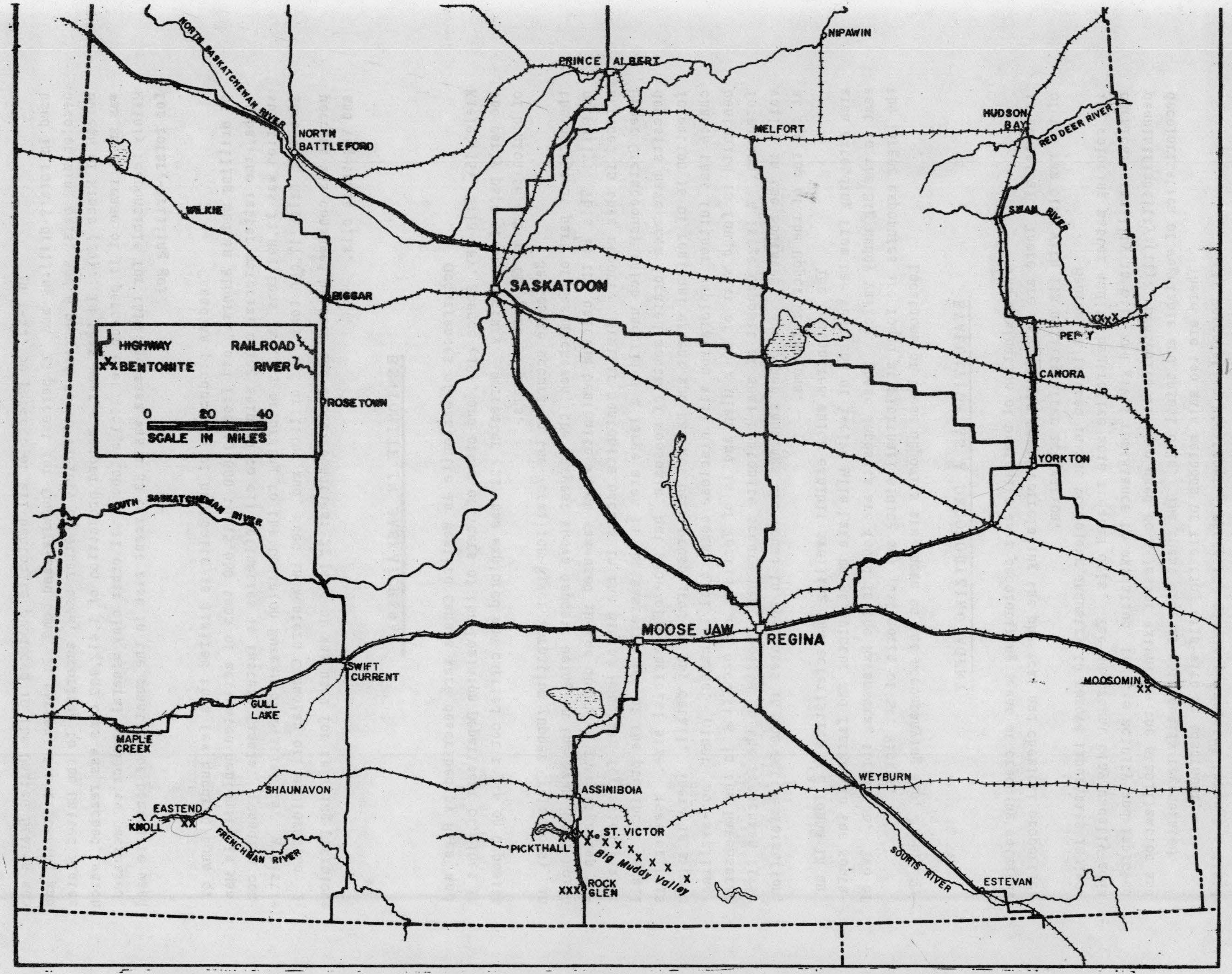
EVALUATION AS A DECOLORIZING AGENT

The evaluation of bentonite as a decolorizing agent or cracking catalyst is empirical. There are no definite tests correlating the physical and chemical properties of the raw clay with its ability after activation.

Bentonite is used in the petroleum industry to remove impurities including coloring matter and to neutralize acid treated oils. The adsorbent clay usually adds chemical stability in oils and gives resistance to oxidation, reduces acidity and improved demulsifiability (11). Bentonite is also used to a lesser extent in the stabilization and decolorization of vegetable and animal oils. The spent clay is not usually regenerated.

There are two main methods of treating oils with an adsorbent:

(1) Percolation treatment - where the oil is percolated through a fixed bed of the adsorbent.



1-7-22-W3

Fig. 2 Southern Saskatchewan showing the location of major bentonite deposits.

(2) Contact treatment - where the adsorbent and oil are intimately mixed at elevated temperatures and in some cases, at elevated pressures.

The contact method is used in Canadian lubricating oil plants.

Bentonites suitable as decolorizing clays are usually acid treated, increasing the activity of the clay many fold. In the United States sulphuric acid is generally used for activation, while hydrochloric acid is the most common acid used in Germany (7).

To evaluate a bentonite as a decolorizing agent, the sample is activated by acid leaching under various conditions of acid concentration, temperature, and duration of treatment. The treated clay is filtered, washed, dried and ground. It is then used to decolorize a standard oil and the reduction in color is measured. This result is compared to the results obtained by decolorizing the oil with a commercial product of known quality.

EVALUATION AS A CRACKING CATALYST

At least some clays suitable for oil decolorization are also used as a cracking catalyst (17, 21). Sinclair Refining Company uses an activated bentonite at its Wellesville, New York plant for decolorizing a lubricating oil. The clay is then shipped 200 miles to its cracking plant at Marcus Hook, Pennsylvania (21).

The natural clay catalyst may be used as a carrier impregnated with some other catalytic material. The present trend is to use the clay catalyst alone in the fluid catalytic cracking process. Because of the even distribution of the catalyst and other reasons, the entire cracking operation can be kept at exact temperatures. The coke and tar formed on the catalyst are burned off during the regeneration cycle.

The advantage of the catalytic cracking process is that the oil is heated to lower temperatures and pressures than in other types of cracking processes such as thermal cracking, and high yields of motor fuels with high octane numbers are obtained.

Although the decolorization test required relatively simple equipment, a test for determining the quality of a cracking catalyst is much more complex. The Cat 'A' test, which is one of the generally accepted standard tests, involves cracking of a petroleum fraction and identification of the products. The equipment for this test is available only in some of the larger laboratories.

Since the determination is costly, it is wise to limit the number of samples to be tested. Accordingly a 'screening test' was conducted to select encouraging samples only for further study. In his study of bentonite Thomas (19) showed that a relationship existed between the acidity of the activated clay and its cracking efficiency. The acidity value determined by potassium hydroxide titration, reached a maximum with increasing severity of treatment then either decreased or remained constant (19). Acidity values, then, would indicate in a preliminary way those samples having the greater catalytic activity.

Mills et al (12) also related the activity of a bentonite catalyst to the portion of R_2O_3 removed during activation, and found that the best product was obtained when about 50% was removed. Thomas and co-workers (19) showed that optimum activity is gained when about half the central layer atoms in the montmorillonite are removed. This is in agreement with Mills, and the R_2O_3 removal would serve as a check on the optimum conditions for clay preparation.

PRELIMINARY EXPERIMENTS

Nutting (14) has discussed the activation of American bentonites. Activation of Canadian bentonites by sulphuric acid leaching for decolorization purposes has been described by Gallay (8), and Worcester (22). The work described here was initiated by Jessup (10) who first used sulphuric acid for activation several Saskatchewan bentonites with only moderate success. Much better results were obtained when the bentonites were activated with hydrochloric acid.

In his investigation of Canadian bentonites, Dr. Gallay found that drying bentonites at temperatures above 200 deg C decreased the adsorbent quality. Drying should be effected at temperatures below 200 deg C and the moisture content before activation should not fall below a certain critical level. This is confirmed by Mukherjee and Roy (13). The method of activation adopted was to dry the raw bentonite slowly to approximately 16-18% moisture content. At this water content the clay could be ground easily in a Mikropulverizer and still remain above the critical moisture content, which was found to be about 12%. Below this, the efficiency of the clay was impaired.

One hundred grams (dry basis) of the dried ground bentonite (80% minus 200 mesh) was then added to a flask containing 250 ml of a 1:1 hydrochoric acid solution. The mixture was refluxed for two hours and the product filtered and washed until pH of 3.5 - 4.0 was reached. The activated clay was then dried overnight at 45-50 deg C and reground in the pulverizer to 80% minus 200 mesh.

The initial method of testing the decolorizing power of the clays was rapid and simple: 150 grams of undecolorized SAE 30 oil was weighed out into a 400 ml glass beaker and 6% by weight of activated clay was added. The beaker was put on a hot plate, the mixture stirred mechanically and the temperature allowed to rise to 150 deg C in 15 minutes. After cooling for 10 minutes, the mixture was filtered and the transmittance of the oil measured with a Fisher Electrophotometer using a color-in-oil adsorption unit and a 5100 A filter.

In some experiments, conditions were varied in order to obtain additional information which would be of value for future work. Table 1 shows the location and description of the samples, and Table 11 shows the results obtained using the various bentonites.

TABLE 1

GENERAL LOCATION OF BENTONITES TESTED

Sample	Raw Color	General Location
21-S-1	Yellow with iron stains	Pelly
Rock Glen	White	Rock Glen
17-S-1	Grey	St. Victor
51-M-1	Grey	Swift Current
51-M-2	Grey	Swift Current
24A	Grey-grey green	Moosomin
B	Light olive-light grey	Moosomin
C	Grey - very ironstained	Moosomin
D	Light olive grey - olive green	Moosomin

TABLE 11

ACTIVATION AND DECOLORIZING TESTS OF SASKATCHEWAN BENTONITES

Sample	Activation		Decolorization		Remarks
	Acid Used	% Loss of Weight	% Clay	% Transmittance	
Raw SAE 30 oil	-	-	-	54.0	
Commercial Clay	-	-	4	81.8	
21-S-1	HCl	25	6	96.4	Activ. Clay dried 70 deg C
	HCl	25	6	89.6	Activ. Clay dried 110 deg C
	HCl	-	4	90.5	Activ. Clay dried 43 deg C
	HCl	-	6	90.0	Activ. clay dried 104 deg C
	H_2SO_4	-	6	82.5	
Rock Glen	HCl	22	6	80.5	
17-S-1	HCl	7.4	4	52.3	
51-M-1	HCl	20	4	n.g	
	H_2SO_4	36	4	75.1	
51-M-2	HCl	18	4	n.g	
	H_2SO_4	38	4	75.0	
24A	HCl	18	4	-	Activation incomplete
	HCl	22.6	4	93.2	
24B	HCl	20.0	4	83.5	
	HCl	24.8	4	93.2	
24C	HCl	20.0	4	83.0	
	HCl	25.5	4	83.2	
24D	HCl	21.5	4	78.7	
	HCl	25.3	4	81.5	

DETAILED EXPERIMENTS ON BENTONITE 21-S-1

Bentonite 21-S-1 and the samples from Moosomin (24A and B) showed the highest decolorizing efficiency. Although the tests showed both to be of similar quality, only a small quantity of the Moosomin bentonite has been located, so further detailed work was done on 21-S-1 from the Pelly deposit. Drilling and excavating has indicated a substantial quantity of bentonite at this location (5) but the beds are badly folded, making an estimate of tonnage very difficult.

Chemical and differential thermal analyses were performed and the results are compared to American Petroleum Institute (1) standard bentonites in Table 111 and Figure 3.

TABLE 111

CHEMICAL ANALYSES OF 21-S-1 AND AMERICAN BENTONITES

Percent by weight

Component	1	2	3
SiO_2	62.0	63.5	59.4
Al_2O_3	19.6	21.3	20.4
TiO_2		0.13	0.29
Fe_2O_3	4.71	3.53	2.92
CaO	2.23	0.27	2.74
MgO	3.94	2.88	4.10
Na_2O	0.75	1.83	0.17
K_2O	0.34	0.34	0.33
Ignition Loss	6.46	6.75	9.15
TOTAL	100.0	100.6	99.5

1. Calcium Bentonite 21-S-1, Pelly, Sask.
2. Sodium Bentonite, A.P.I. reference mineral 27, Belle Fourche, South Dakota (Report 7, p. 54).
3. Calcium Bentonite, A.P.I. reference mineral 23, Chambers, Arizona (Report 7, p. 53).

Note: A.P.I. analyses have been recalculated to a water-free at 110°C basis for comparison with Saskatchewan analyses. Ferrous and ferric iron are included in Fe_2O_3.

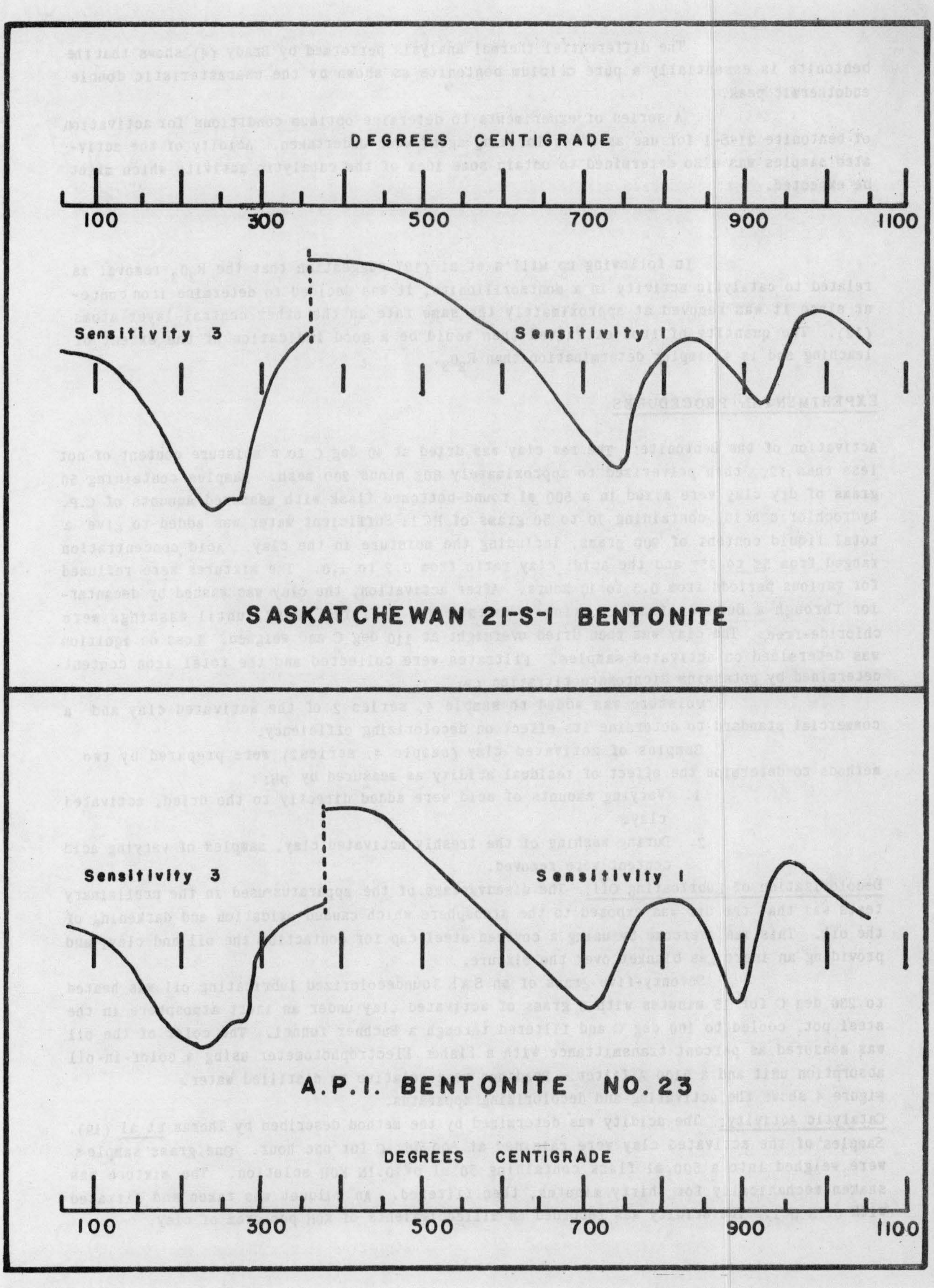


FIGURE 3. THERMOGRAMS OF BENTONITES (4).

The differential thermal analysis performed by Brady (4) shows that the bentonite is essentially a pure calcium bentonite as shown by the characteristic double endothermic peak.

A series of experiments to determine optimum conditions for activation of bentonite 21-S-1 for use as a decolorizing agent were undertaken. Acidity of the activated samples was also determined to obtain some idea of the catalytic activity which might be expected.

In following up Mill's et al (12) suggestion that the R_2O_3 removal is related to catalytic activity in a montmorillonite, it was decided to determine iron content since it was removed at approximately the same rate as the other central layer atoms (12). The quantity of iron extracted then would be a good indication of the extent of leaching and is a simpler determination than R_2O_3.

EXPERIMENTAL PROCEDURES

Activation of the Bentonite: The raw clay was dried at 40 deg C to a moisture content of not less than 12%, then pulverized to approximately 80% minus 200 mesh. Samples containing 50 grams of dry clay were mixed in a 500 ml round-bottomed flask with measured amounts of C.P. hydrochloric acid, containing 10 to 50 grams of HCl. Sufficient water was added to give a total liquid content of 200 grams, including the moisture in the clay. Acid concentration ranged from 5% to 25% and the acid: clay ratio from 0.2 to 1.0. The mixtures were refluxed for various periods from 0.5 to 10 hours. After activation, the clay was washed by decantation through a Buchner funnel, using a Whatman No. 4 filter paper, until washings were chloride-free. The clay was then dried overnight at 110 deg C and weighed. Loss on ignition was determined on activated samples. Filtrates were collected and the total iron content determined by potassium dichromate titration (2).

Moisture was added to sample 4, series 2 of the activated clay and a commercial standard to determine its effect on decolorizing efficiency.

Samples of activated clay (sample 4, series 2) were prepared by two methods to determine the effect of residual acidity as measured by pH:

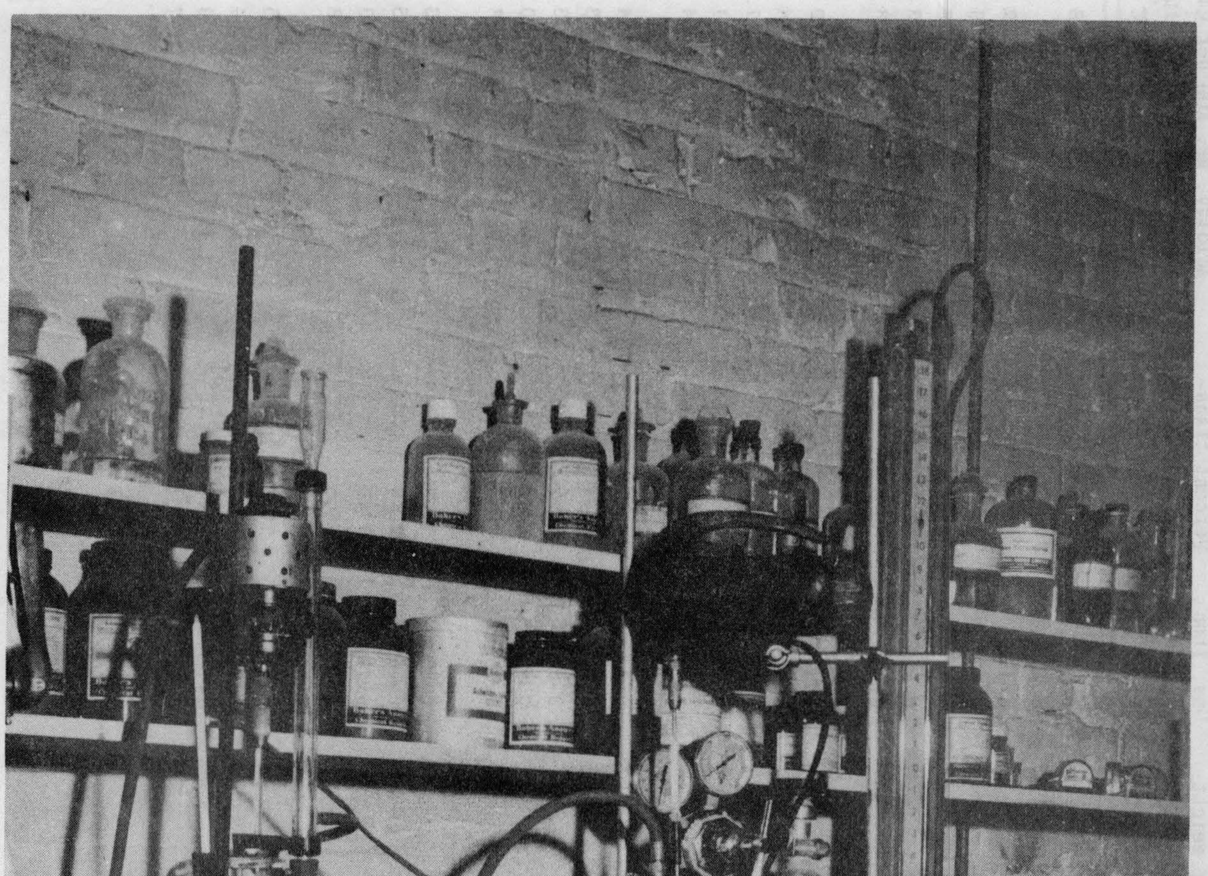
1. Varying amounts of acid were added directly to the dried, activated clay.
2. During washing of the freshly activated clay, samples of varying acid content were removed.

Decolorization of Lubricating Oil: The disadvantage of the apparatus used in the preliminary tests was that the oil was exposed to the atmosphere which caused oxidation and darkening of the oil. This was overcome by using a covered steel cup for contacting the oil and clay, and providing an inert gas blanket over the mixture.

Seventy-five grams of an SAE 30 undecolorized lubricating oil was heated to 230 deg C for 15 minutes with 3 grams of activated clay under an inert atmosphere in the steel pot, cooled to 100 deg C and filtered through a Buchner funnel. The color of the oil was measured as percent transmittance with a Fisher Electrophotometer using a color-in-oil absorption unit and a 5100 A filter. Readings were relative to distilled water.

Figure 4 shows the activating and decolorizing apparatus.

Catalytic Activity: The acidity was determined by the method described by Thomas et al (19). Samples of the activated clay were calcined at 500 deg C for one hour. One grams samples were weighed into a 500 ml flask containing 50 ml of 0.1N KOH solution. The mixture was shaken mechanically for thirty minutes, then filtered. An aliquot was taken and titrated with 0.1N HCl. The acidity was recorded as millequivalents of KOH per gram of clay.



SASK. D.N.R. PHOTO

FIGURE 4 - ACTIVATING AND DECOLORIZING APPARATUS

TABLE 1V

EFFECT OF LEACHING SASKATCHEWAN BENTONITE 21-S-1 WITH HYDROCHLORIC ACID

Series No.	Sample No.	Activation Period, hrs.	Acid Conc. % by weight	Acidid: clay by weight	% Loss of weight during activation (dry Basis, 110°C)	Gms. Iron leached, per 50 gm	Percent transmittance decolorized oil	Acidity, me. KOH per gm. clay	
								Before calcining	Calcined 500°C
1	1	0.5	5%	0.2	2.8	0.40	64.4		0.36
	2	1.0			4.0	0.40	72.3	1.39	-
	3	2.0			6.4	0.46	74.1	1.40	0.60
	4	3.5			6.6	0.50	78.7	1.30	0.69
	5	5.0			7.9	0.54	82.1	1.42	0.78
	6	7.0			8.0	0.57	86.0	1.42	0.78
	7	10.0			11.2	0.60	86.0		1.08
2	1	0.5	10%	0.4	6.2	0.47	74.7		0.40
	2	1			8.2	0.48	75.5	1.39	0.54
	3	2			9.1	0.55	82.6		0.67
	4	3.5			13.2	0.70	86.7	1.39	0.81
	5	5			14.8	0.87	85.2	1.39	0.84
3	1	0.5	15%	0.6	7.5	0.37	78.0	1.21	0.54
	2	1			8.6	0.47	83.4	1.21	0.63
	3	2			13.2	0.50	84.5		0.83
	4	3.5			18.6	0.83	84.0	1.21	1.00
	5	3.0			20.7	1.20	78.5		1.08
4	1	0.5	20%	0.8	7.4	0.55	77.8	1.19	0.53
	2	1			10.5	0.66	78.9	1.15	0.65
	3	2			17.0	0.78	77.0		1.10
	4	3.5			24.7	1.40	76.5	1.15	0.98
5	1	0.5	25%	1.0	7.5	0.61	76.2	1.15	0.55
	2	1			10.8	0.70	83.5		0.64
	3	2			17.3	0.97	81.6	1.15	0.79
	4	3.5			24.1	1.24	81.4		0.97
SAE 30 lube oil							57.8		
Standard Commercial bentonite							80.6		
Synthetic catalyst									0.87
Commercial clay catalyst									1.67

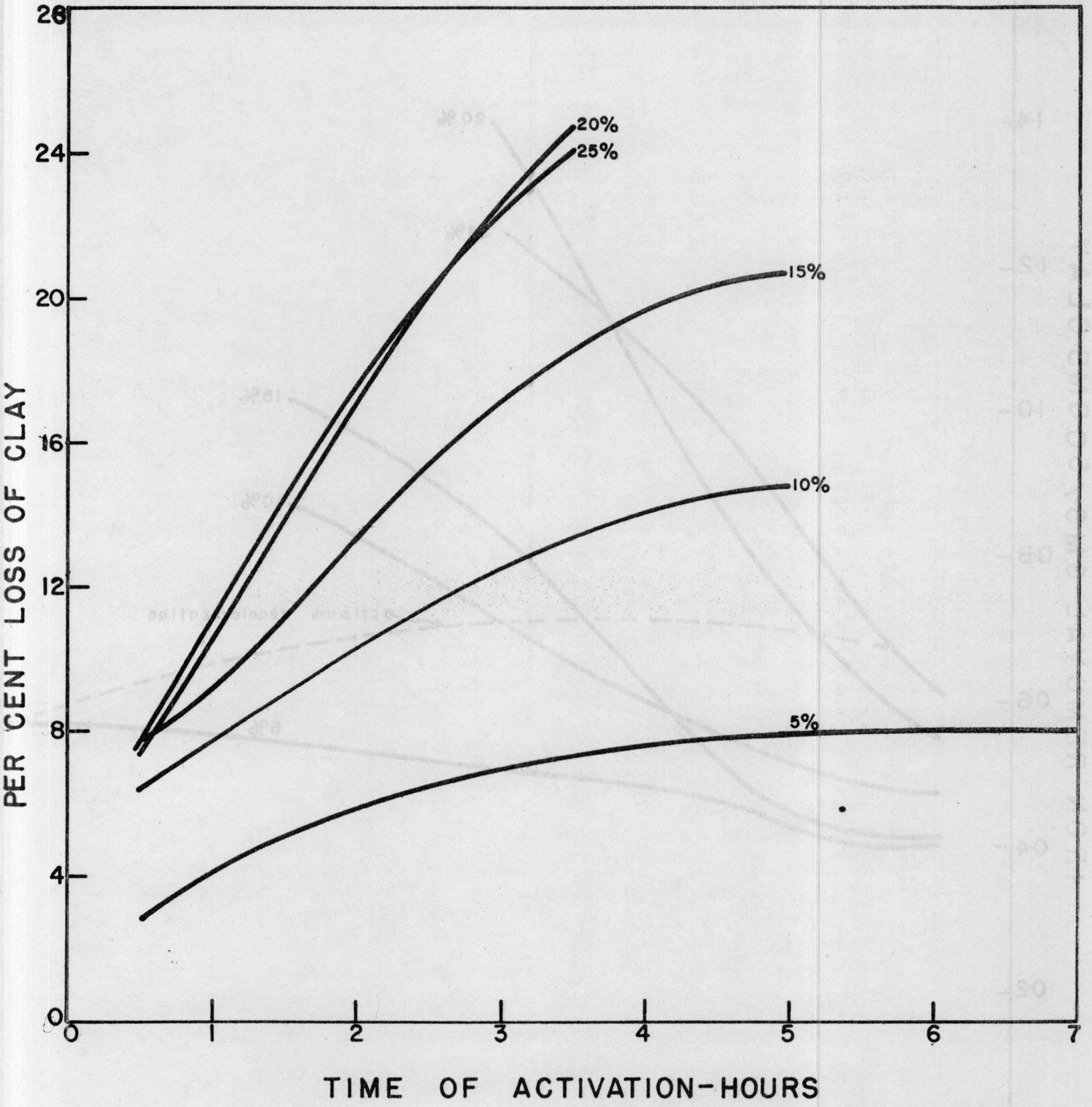


FIGURE 5. REMOVAL OF TOTAL CONSTITUENTS AS A FUNCTION OF TIME AT VARIOUS ACID CONCENTRATIONS.

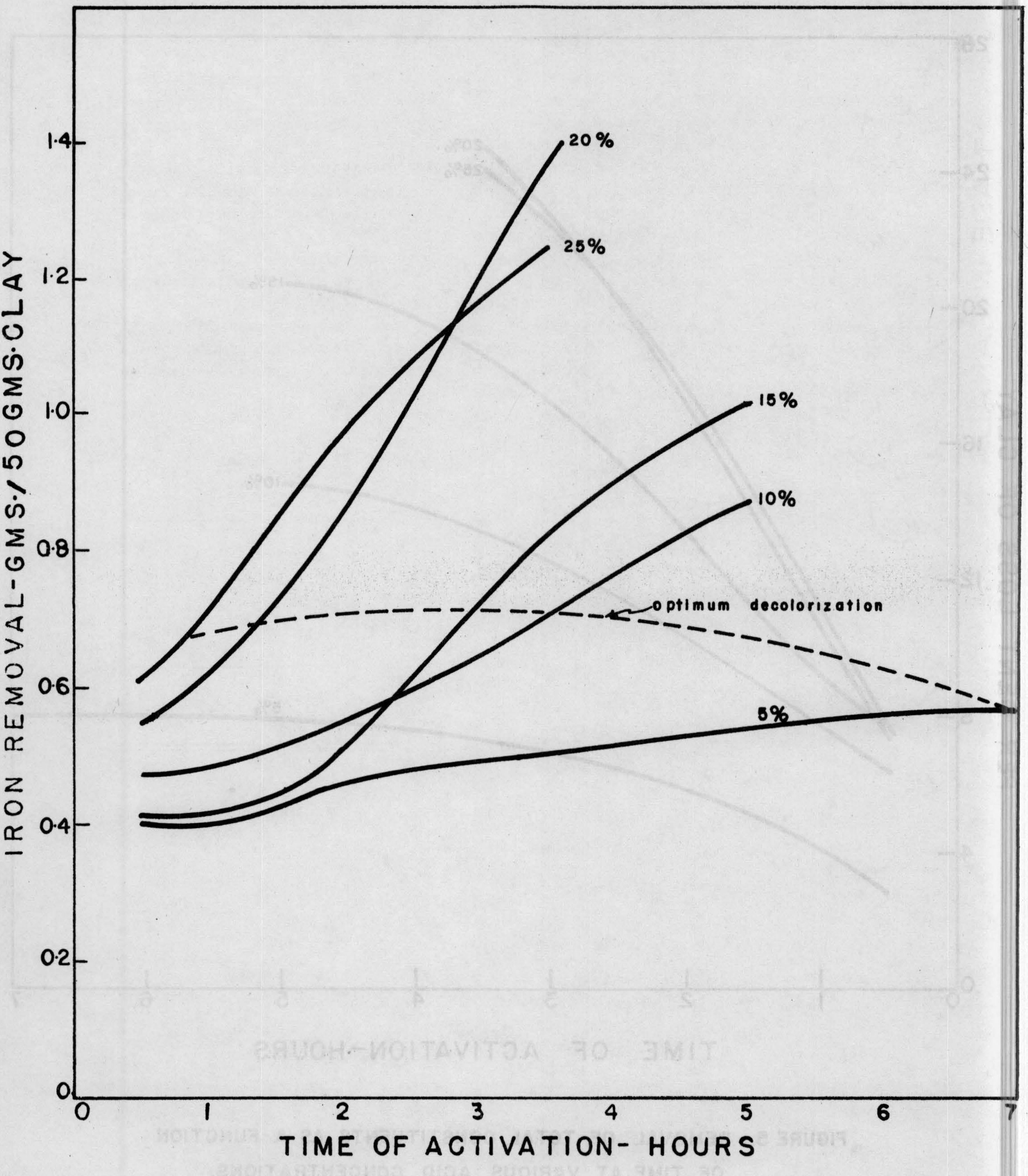


FIGURE 6. IRON REMOVAL AS A FUNCTION OF TIME AT VARIOUS ACID CONCENTRATIONS.

RESULTS AND DISCUSSION

The data on the effect of leaching the 21-S-1 bentonite under various conditions, its decolorizing power and acidity are compiled in Table 1V. Bhola (3) stated that a direct relationship exists between decolorizing action and exchangeable hydrogen ion. No such relationship was found as can be seen from Table 1V.

Since the surface area of the activated clay increases with continued acid leaching as noted by Mills et al (12) while decolorizing power passes through a maximum as seen in Figure 8, some fundamental factor other than surface area must be involved in decolorization.

One gram samples of dried (110 deg C) activated bentonite were weighed out, then put in a muffle furnace and heated to 950 deg C. At this temperature the montmorillonite structure has been destroyed and along with it any adsorbing properties.

The absolute values of the ignition loss (combined water or hydroxyl groups) apparently bear no relation to one another when compared to the decolorizing power as shown in Table V. However, in each series the hydroxyl content passes through a maximum. In every case, the optimum percent transmittance coincides with this maximum.

Referring to Figures 5 and 6, it can be seen that total clay and iron loss increased with increased leaching time as expected. In the extreme a silica skeleton is left (12). Generally a greater concentration of acid will also leach more material in the same time.

TABLE V

CHEMICALLY BOUND MOISTURE REMOVED AT 950^{o}C

(Initial Drying Temperature 160^{o}C)

Acid Conc. Percent	Sample	Ignition Loss (OH Loss) %	% Transmittance
5%	Series 1 - 2	7.02	74.1
	3	7.00	78.7
	4	8.77	86.0
	5	6.74	86.0
10%	Series 2 - 2	6.80	75.5
	4	7.44	86.7
	5	7.19	85.2
15%	Series 3 - 1	6.75	78.0
	2	6.50	83.4
	3	8.15	84.5
	4	6.20	84.0
20%	Series 4 - 1	7.11	77.8
	2	7.54	78.9
	4	6.56	76.5
25%	Series 5 - 1	6.40	76.2
	2	7.45	83.5
	3	5.55	81.6

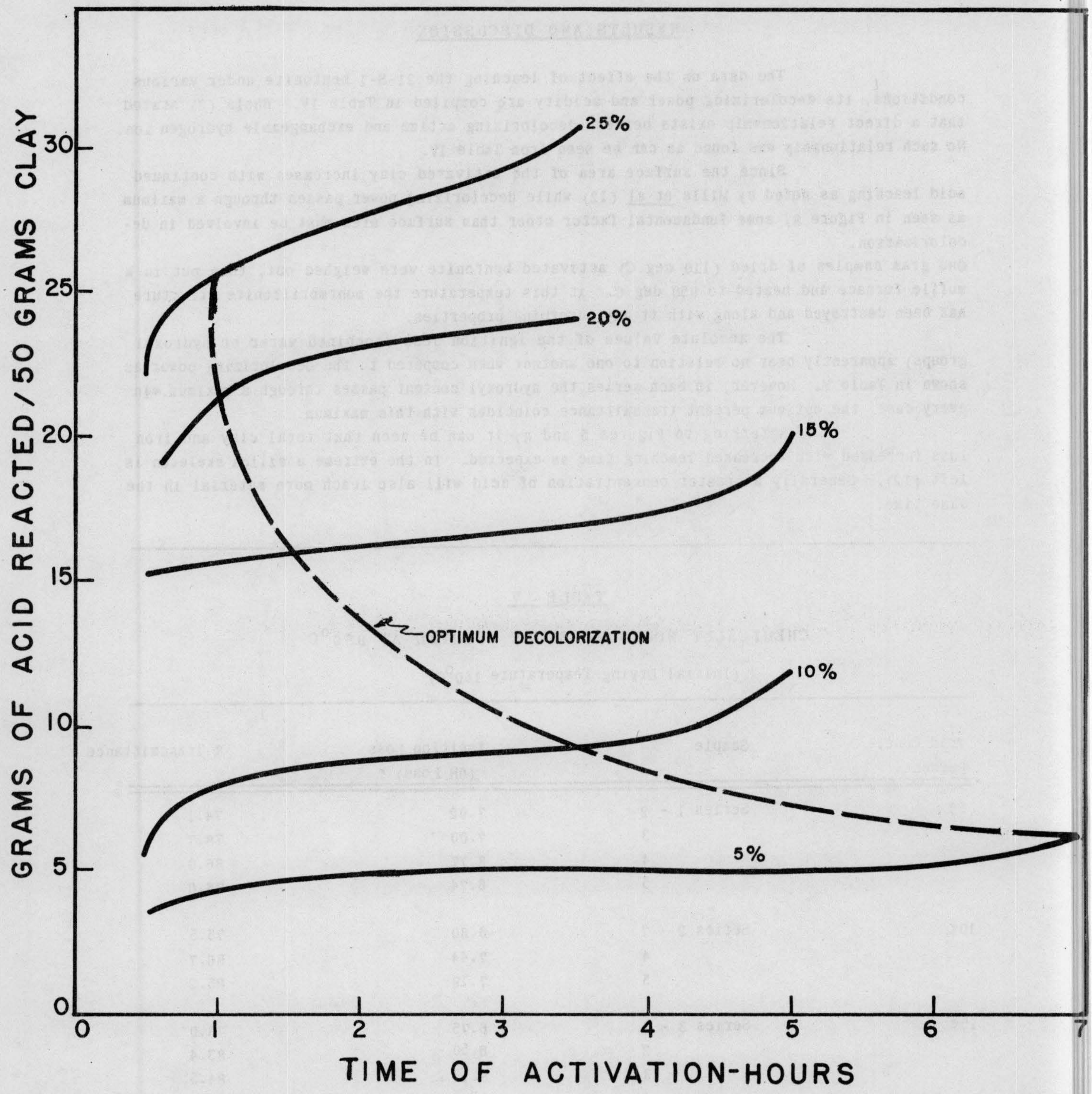


FIGURE 7. ACID CONSUMPTION AS A FUNCTION OF TIME AT VARIOUS ACID CONCENTRATIONS.

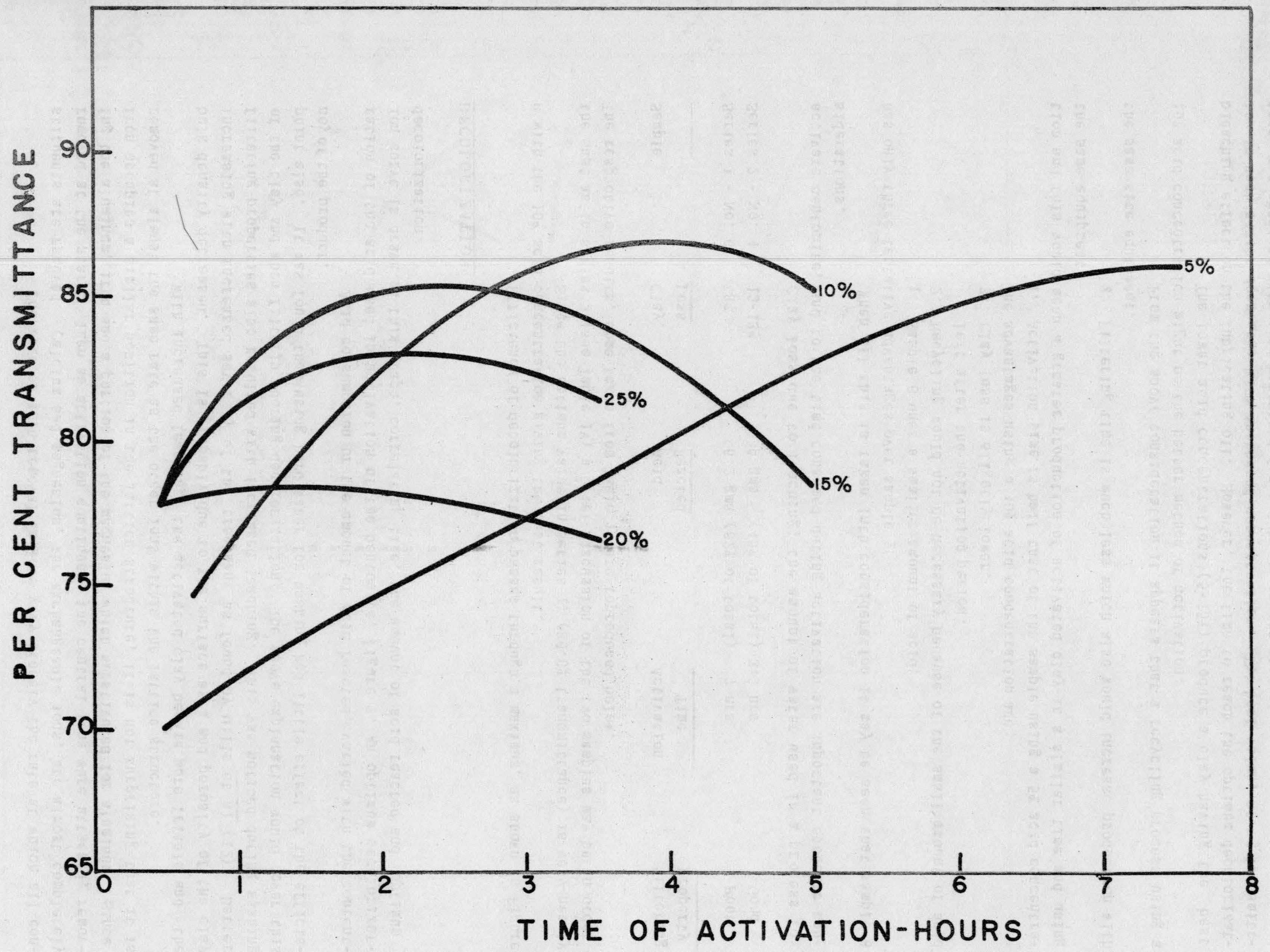


FIGURE 8. DECOLORIZING POWER AS A FUNCTION OF ACTIVATION TIME AT VARIOUS ACID CONCENTRATIONS.

The rate of iron removal follows very closely the rate at which all constituents are removed. Calcium and magnesium, the exchangeable ions, are almost completely removed at the start. Then as activation continued, the central ions were attacked, removing the aluminum, iron and a portion of the magnesium which substituted for aluminum. Since iron occupies a similar position in the lattice structure, it is not surprising that it is removed at almost the same rate as the other ions within the lattice structure.

With increased leaching, the activated clay became more friable and the bulk density decreased. This is probably due to the surface area and porosity of the clay increasing with increased severity of the treatment as found by Mills et al (12). Better filtering properties also resulted with increased leaching. This was noticed during washing of the clay and when filtering during decolorization. The above explanation would cover this point also. It was found that using hard water for washing had little effect on the efficiencyof the product.

Acid consumption or the amount of acid reacted, varied with the contentration of the acid used in activation of the bentonite, Figure 7. An optimum decolorization curve is drawn on this graph, correlating time, the amount of acid reacted and optimum decolorization.

DECOLORIZATION

Efficiency of decolorization passes through a maximum, as shown in Figure 8 with the 10% acid concentration giving the best result.

Since the optimum value in series 1, (86.0% transmittance) is very nearly the same as in series 2 (see Table 1V) a brief discussion of the two samples may be in order. The respective results, some taken from Table 1V are reproduced below.

Sample	Clay Loss	Acid Reacted	Activation Time	Filtering Property
Series 1 - No. 6	8%	6.2 gms (62% of total)	7 hrs	Poor
Series 2 - No. 4	12-13%	9 gms (45% of total)	3.5 hrs	Good

Clay loss due to leaching, the amount of water used in a process to activate bentonite, and to the time consumed during activation are important economic considerations.

When all this is taken into consideration it may be seen that sample 6 has only three tentative advantages over sample 2:

1. Sample 6 uses a smaller amount of acid.
2. Recycling would not be necessary because of the small amount of acid left after the activation period.
3. Clay loss is slightly lower.

The advantages using a 10% acid concentration are:

1. Activation time is half that of the sample using a 5% acid concentration and this would mean a greater production of activated clay in a similar time and using the same equipment.

2. Filtering time is much less which also would increase production with the same size equipment.

From the above consideration it appears that a recycling process using a 10% acid concentration might be the better method of activation.

The lower acid concentrations (5-15%) produce a clay having the best bleaching effect on the lubricating oil. However, the time to reach the optimum decolorization in each series decreases with increased concentration. The best value, 86.7% transmittance, was obtained with clay activated for 3.5 hours in 10% acid.

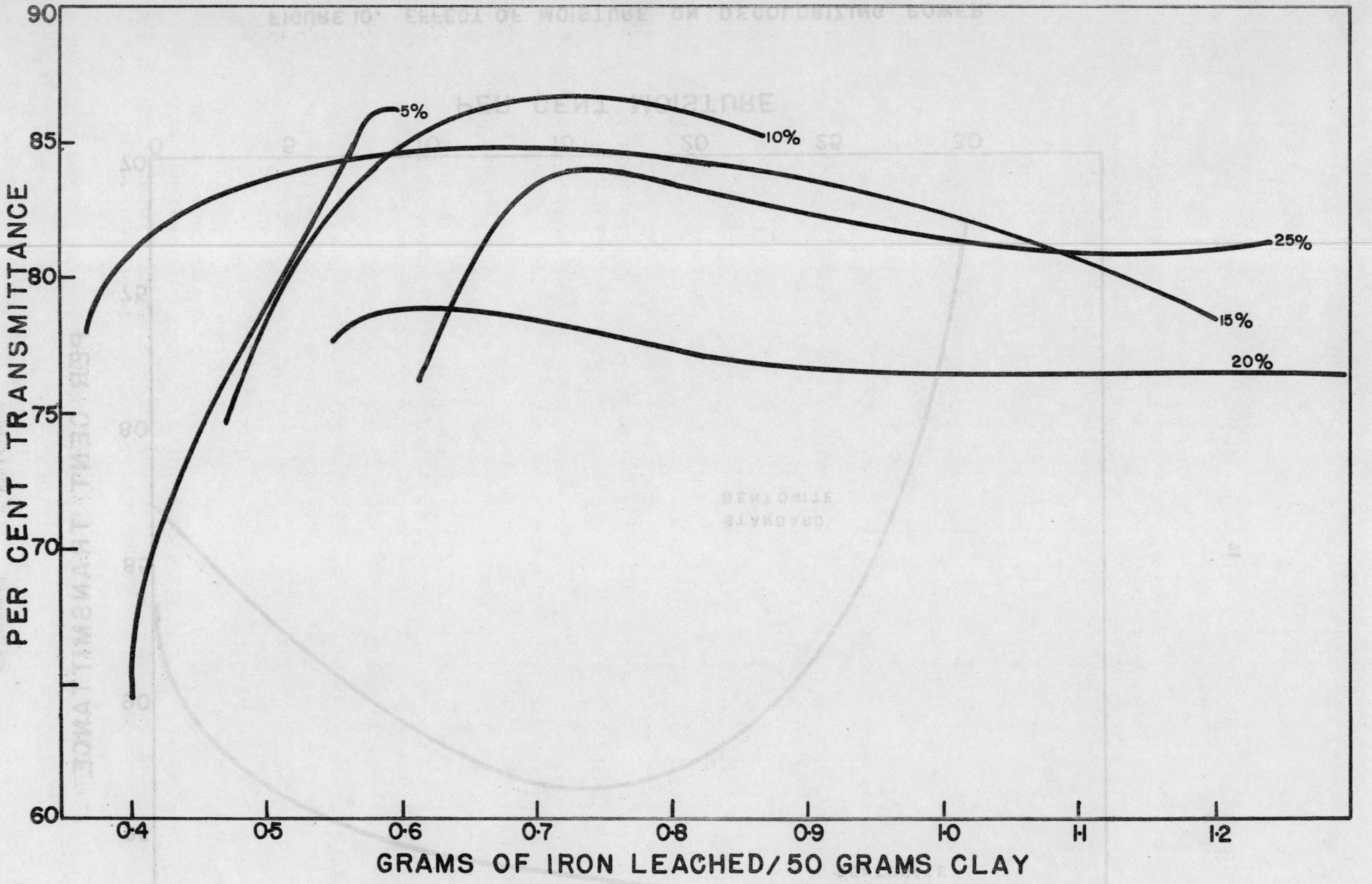


FIGURE 9. EFFECT OF IRON REMOVAL ON DECOLORIZING POWER AT VARIOUS ACID CONCENTRATIONS.

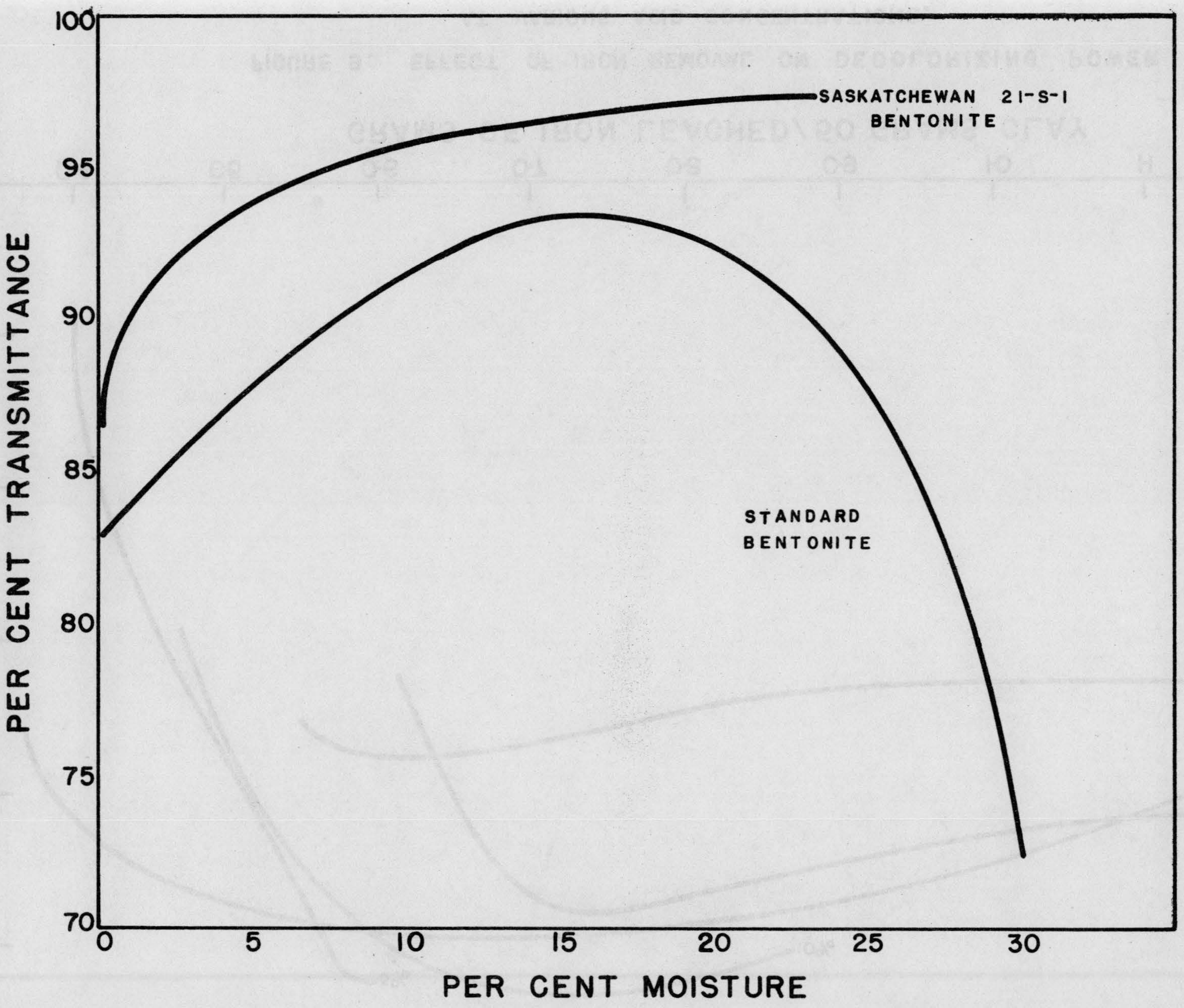


FIGURE 10. EFFECT OF MOISTURE ON DECOLORIZING POWER.

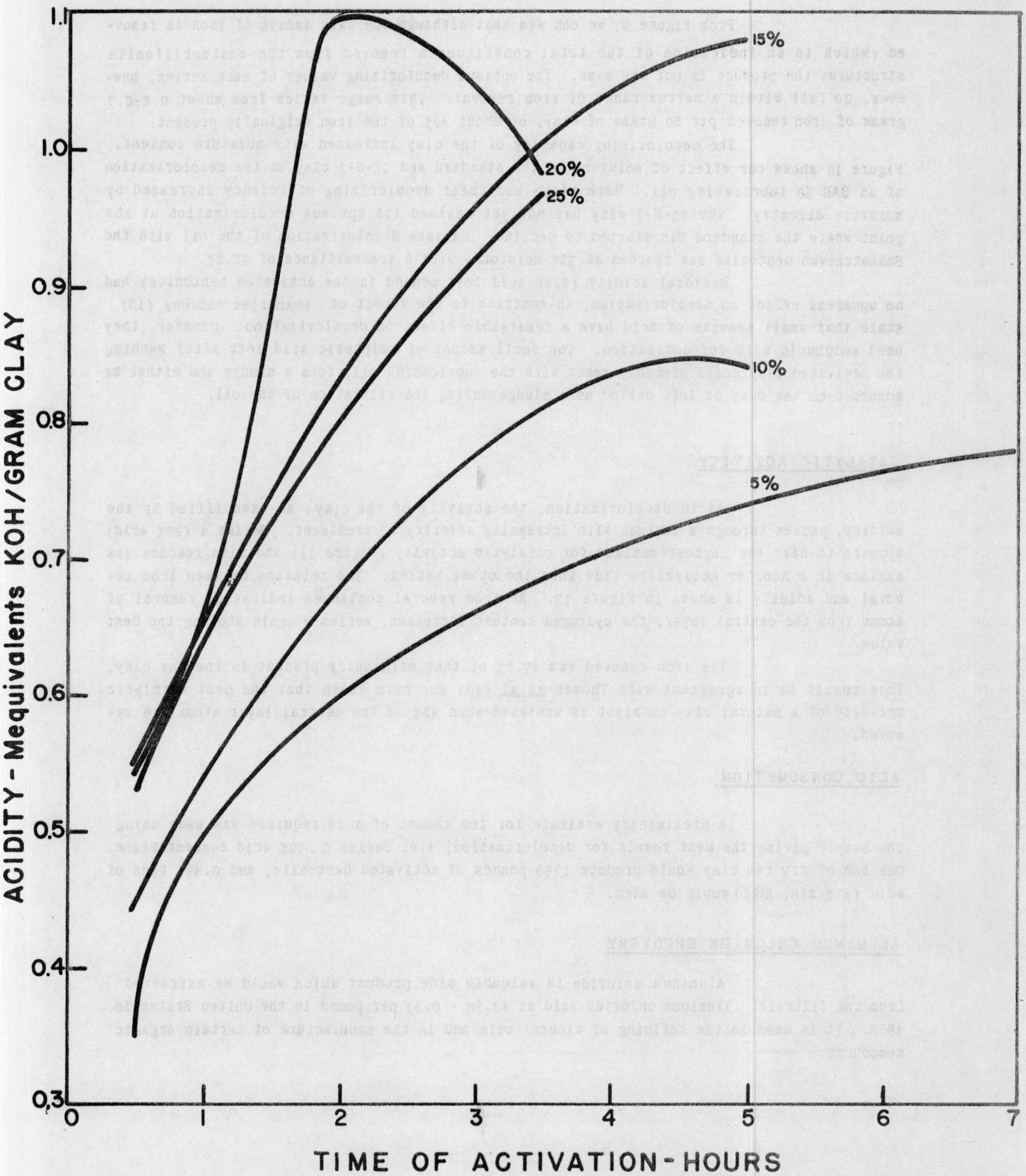


FIGURE 11. ACIDITY OF ACTIVATED BENTONITE AS A FUNCTION OF TIME AT VARIOUS ACID CONCENTRATIONS.

From Figure 9, we can see that although the same amount of iron is removed (which is an indication of the total constituents removed from the montmorillonite structure) the product is not the same. The optimum decolorizing values of each series, however, do fall within a narrow range of iron removal. This range varies from about 0.6-0.7 grams of iron removed per 50 grams of clay, or about 40% of the iron originally present.

The decolorizing capacity of the clay increased with moisture content. Figure 10 shows the effect of moisture in the standard and 21-S-1 clay on the decolorization of an SAE 30 lubricating oil. Both clays had their decolorizing efficiency increased by moisture directly. The 21-S-1 clay has not yet reached its optimum decolorization at the point where the standard has started to decline. Maximum decolorization of the oil with the Saskatchewan bentonite was reached at 23% moisture, with a transmittance of 97.5%.

Residual acidity (free acid left behind in the activated bentonite) had no apparent effect on decolorization, in contrast to the report of Mukherjee and Roy (13) state that small amounts of acid have a remarkable effect on decolorization. However, they used sulphuric acid for activation. The small amount of sulphuric acid left after washing the activated clay could probably react with the lubricating oil, form a sludge and either be adsorbed on the clay or left behind as a sludge during the filtration of the oil.

CATALYTIC ACTIVITY

As in decolorization, the activity of the clay, as exemplified by the acidity, passes through a maximum with increasing severity of treatment. Series 4 (20% acid) appears to have the highest maximum for catalytic activity (Figure 11) and also reaches its maximum in a shorter activation time than the other series. The relation between iron removal and acidity is shown in Figure 12. As iron removal continues indicating removal of atoms from the central layer, the hydrogen content increases, series 4 again showing the best value.

The iron removed was 47.5% of that originally present in the raw clay. This result is in agreement with Thomas et al (19) who have shown that the best catalytic activity of a natural clay catalyst is achieved when 45% of the central layer atoms are removed.

ACID CONSUMPTION

A preliminary estimate for the amount of acid required was made using the sample giving the best result for decolorization, i.e. Series 2, 10% acid concentration. One ton of dry raw clay would produce 1760 pounds of activated bentonite, and 0.497 tons of acid (37% min. HCl) would be used.

ALUMINUM CHLORIDE RECOVERY

Aluminum chloride is valuable side product which would be extracted from the filtrate. Aluminum chloride sold at $0.28 - 0.30 per pound in the United States in 1953. It is used in the refining of mineral oils and in the manufacture of certain organic compounds.

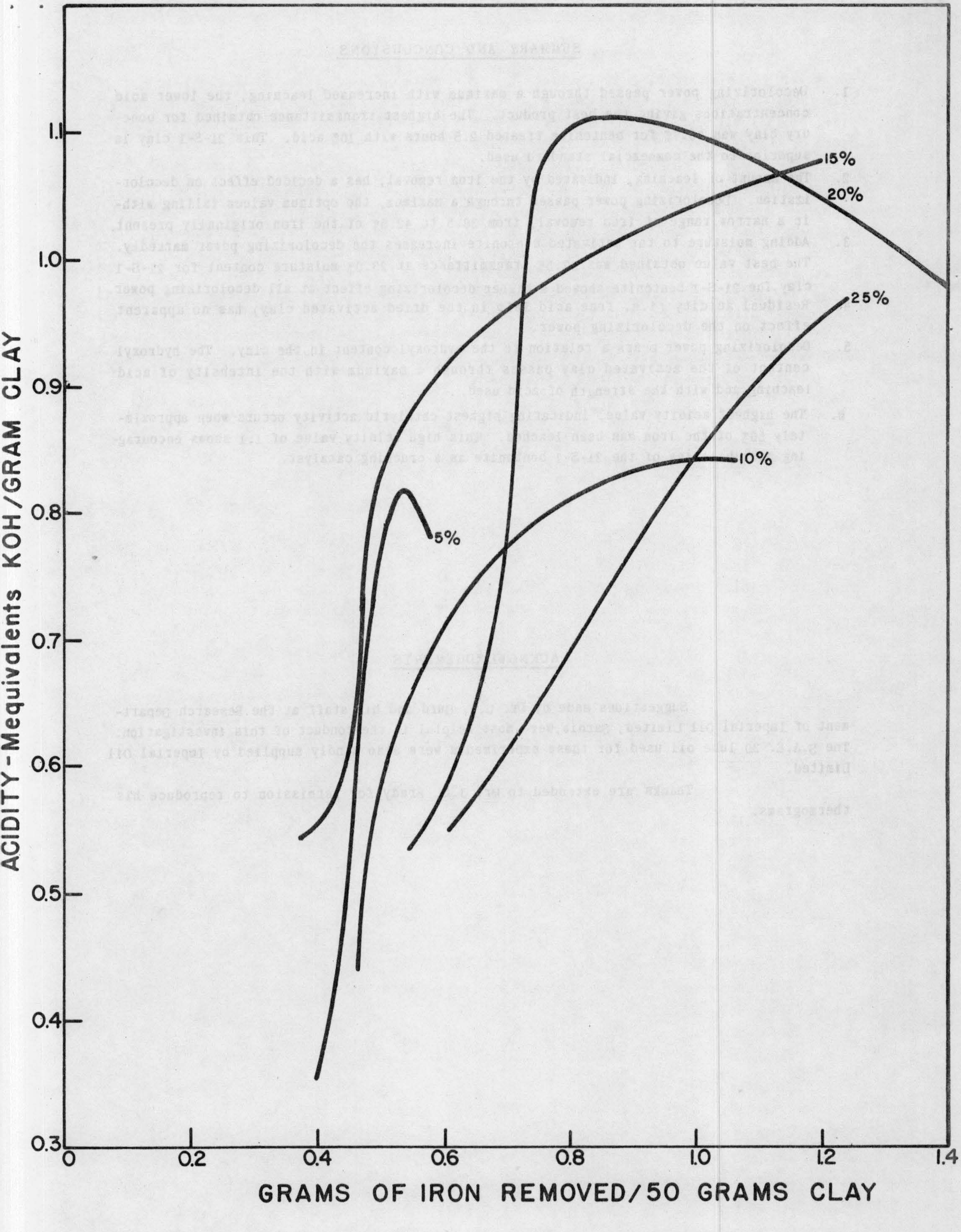


FIGURE 12. ACIDITY OF ACTIVATED BENTONITE AS A FUNCTION OF IRON REMOVAL AT VARIOUS ACID CONCENTRATIONS

SUMMARY AND CONCLUSIONS

1. Decolorizing power passed through a maximum with increased leaching, the lower acid concentrations giving the best product. The highest transmittance obtained for bone-dry clay was 86.7% for bentonite treated 2.5 hours with 10% acid. This 21-S-1 clay is superior to the commercial standard used.
2. The amount of leaching, indicated by the iron removal, has a decided effect on decolorization. Decolorizing power passes through a maximum, the optimum values falling within a narrow range of iron removal, from 36.5 to 42.5% of the iron originally present.
3. Adding moisture to the activated bentonite increases the decolorizing power markedly. The best value obtained was 97.5% transmittance at 23.0% moisture content for 21-S-1 clay.The 21-S-1 bentonite showed a higher decolorizing effect at all decolorizing power.
4. Residual acidity (i.e. free acid left in the dried activated clay) has no apparent effect on the decolorizing power.
5. Decolorizing power bears a relation to the hydroxyl content in the clay. The hydroxyl content of the activated clay passes through a maximum with the intensity of acid leaching and with the strength of acid used.
6. The highest acidity value, indicating highest catalytic activity occurs when approximtely 50% of the iron has been leached. This high acidity value of 1.1 shows encouraging possibilities of the 21-S-1 bentonite as a cracking catalyst.

ACKNOWLEDGEMENTS

Suggestions made by Dr. G.W. Gurd and his staff at the Research Department of Imperial Oil Limited, Sarnia,were most helpful in the conduct of this investigation. The S.A.E. 30 lube oil used for these experiments were also kindly supplied by Imperial Oil Limited.

Thanks are extended to Mr. J.G. Brady for permission to reproduce his thermograms.

REFERENCES

1. American Petroleum Institute, Reference Clay Minerals. A.P.I. Project 49. Columbia University, New York 1951.
2. American Society for Testing Materials Designation: D 718-45. 1945.
3. Bhola, K.L., Trans. Ind. Cer. Soc. 5(3). 104-24 (1946).
4. Brady, J.G., Differential Thermal Analysis of Clay Minerals Master's Thesis. University of Saskatchewan, 1952.
5. Crawford, G.S., and Carlson, E.Y., Core Drilling for Industrial Minerals in Saskatchewan 1948 - 1952. Saskatchewan Department of Mineral Resources. Industrial Mineral Report No. 1, 1953.
6. Ells, S.C., Cretaceous Shales of Manitoba and Saskatchewan. Canada Department of Mines, Memorandum Series No. 3, 1921.
7. FIAT Final Report 810, Activated Clay Bleaching Adsorbents. U.S. Bureau of Mines.
8. Gallay, W., Can. Jour. of Research 16, Sec. B (1938).
9. Grim, Ralph E., Clay Mineralogy. McGraw-Hill Book Co. Inc., New York, 1953.
10. Jessup, W.J., Unpublished Report, Saskatchewan Department of Natural Resources Utilization Laboratory, Regina, Saskatchewan. (1951).
11. Kalichevsky, V.A., and Stagner B.A., Chemical Refining of Petroleum pages 244-311, (1942), Reinhold Publishing Corporation, New York.
12. Mills, G.A., Holmes, James, and Cornelius, E.G., J. Phy. and Colloid Chem. 54, 1170-85 (1950).
13. Mukherjee S., and Roy, J., Indian Soap J. 16. 281-7 (1951).
14. Nutting P.G., U.S. Geological Survey Bull. 928C (1943).
15. Ries, H., and Keele, J., Clay and Shale Deposits of the Western Provinces, Geol. Survey of Canada Mem. 25, 1913: Mem. 66, 1915.
16. Ross, C.A., and Hendricks, S.B., Minerals of the Montmorillonite Group. U.S. Geol. Survey Prof. Paper 205-B; (1945).
17. Sittig, Marshall. Petroleum Refiner 29, No. 11, 125-32 (1950).
18. Spence, Hugh S., Bentonite. Canada Dept. Mines, Rept. No. 626, 1924.
19. Thomas, C.L., Hickey J., and Sticker, G., Ind. and Eng. Chem. 42 No. 5, 886-71 (1950).
20. United States Bureau of Mines, Mineral Market Report MMS No. 2214. Mineral Industry Survey, 1952.
21. Webber, George, Oil Gas J. 49, No. 24, 78-9, 118-20 (1950).
22. Worcester, W.G., Saskatchewan Bentonites. Can. Inst. Min. & Met. Trans. 40, p. 438-451, 1937.