ACTIVATION AND CLARIFYING PROPERTIES OF FURNER’S EARTH—PART I.


INTRODUCTION.

Fuller’s earth is a name given to a variety of clay-like materials, which are known from ancient times to possess in common the property of removing grease and dirt and hence used by fullers for cleansing woollen goods. In recent years, the earth has become a product of great commercial importance, finding use for a variety of purposes, viz., for cleansing cloths, scouring yarns and fine dyed woollen goods, refining vegetable and mineral oils, grease and lard, for the manufacture of pigments, for printing wall-papers and for use in certain toilet preparations. It is a substance of world-wide distribution as can be seen from the bibliography of the world’s clay deposits compiled by Ries (Jour. Am. Ceram. Society, 1925, 8-4, 428-570). Although until recently the industry was confined mainly to the English and American earths, it has now rapidly developed in other countries, for instance, Germany, Italy, Japan and Russia. In India, no systematic study has yet been made of the possibility of developing the industry although, as we have found, some of the Indian earths are as good as English or American earths, either in their original condition or after a suitable treatment in some cases. Extensive deposits occur at Jaipur,* Jodhpur,§ Jaisalmer in Rajputana, near Jubbalpore in the Central Provinces,† Hyderabad (Sind), Mysore,* Kolhapur and Bhawanagar. Deposits are also reported at Bikaner (Oldham, Geol. Sur. India Records, 1886, 19, 160), in Khairpur State (Ferner, Geol. Sur. India Records, 1935 68, 304), at Kapuli (Rajaputana) (La Touche, Geol. Sur. India Memoirs, 1911, 35, 33), Khirthar beds (Sind) and in the Suleman Range (Blanford, Geol. Sur. India Memoirs, 1880, 17, 140). The industry is as yet undeveloped and many of these deposits remain commercially unexploited. The following table surveys the production of fuller’s earth at the major deposits during the period 1924 to 1928 (Clegg, Geol.

* These deposits have now been exhausted.
§ The deposits in Jodhpur State are very rich, producing three kinds of earths: (1) bentonite from Hati-ki-Dhani, (2) Fuller’s earth from Dip-ki-Dhani and (3) Fuller’s earth from Kapurdi. The first two are probably of Jurassic age and the last-named is found overlying Barmer Sandstone of Cretaceous age. † These deposits occur in the Murwara Tahsil and overlie limestone of the lower Vindhyan range. They are mined by Messrs. G. H. Cook & Sons of Katni,
### Average Tons and Value

<table>
<thead>
<tr>
<th>Source</th>
<th>1924 Tons</th>
<th>1925 Tons</th>
<th>1926 Tons</th>
<th>1927 Tons</th>
<th>1928 Tons</th>
<th>Average Tons</th>
<th>Average Rs.</th>
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<tr>
<td><strong>Central Provinces:</strong></td>
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<tr>
<td>Jubbulpore</td>
<td>19</td>
<td>59</td>
<td></td>
<td>35</td>
<td>76</td>
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<td>186</td>
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<td>Mysore</td>
<td>2,531</td>
<td>143</td>
<td>1,479</td>
<td>214</td>
<td>457</td>
<td>965</td>
<td>1,117</td>
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<td><strong>Rajputana:</strong></td>
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<tr>
<td>Bikaner</td>
<td>450</td>
<td>1,118</td>
<td>918</td>
<td>1,459</td>
<td>1,836</td>
<td>1,171</td>
<td>6,991</td>
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<td>Jaisalmer</td>
<td>5</td>
<td>20</td>
<td>21</td>
<td>36</td>
<td>25</td>
<td>19</td>
<td>283</td>
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<tr>
<td>Jodhpur</td>
<td>1,070</td>
<td>69</td>
<td>1,038</td>
<td>977</td>
<td>1,000</td>
<td>796</td>
<td>13,127</td>
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<tr>
<td><strong>Total</strong></td>
<td>4,078</td>
<td>2,198</td>
<td>3,456</td>
<td>2,718</td>
<td>3,394</td>
<td>3,169</td>
<td>21,706</td>
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*Sur. India Records, 1930, 68, 304*). The outputs have been sporadic and consumed mostly locally. The latest available figure for fuller’s earth and allied clay imports is Rs. 80,355 during the year 1929. If, however, the extensive nature of the Indian deposits and their quality are taken into consideration, there is no reason why any fuller’s earth should be imported at all.

Fuller’s earth occurs in beds in sedimentary rocks belonging to various geological periods ranging from the Silurian to the Eocene. The nature of formation of these deposits is still a matter of speculation. The geologists have, however, agreed that while kaolinitic clays are derived from felspathic rocks, the original source of the sedimentary material which has been transformed into fuller’s earth was such basic rock as amphibole, augite, hornblende, etc. According to one theory, the sedimentary deposits destined to be fuller’s earth were deposited parallel to the ancient shore lines in shallow seas and in the inland lakes, whose beds subsequently underwent continental subsidences and elevations. When the major oscillations were concluded resulting in the shift of the shore lines, incessant surface and sub-surface erosions have materially changed the nature of the beds, particularly those situated near about the underground water level. It is seen that those deposits which are relatively little overburdened and situated near about the underground water level are the best for bleaching purposes, while surface deposits found on high hills are locally changed into flint sand and siliceous rocks, and those
underneath the present water level have remained unactivated due to the impervious nature of the hard-pans and are therefore of an inferior quality. Activation is supposed to be effected due to percolation of surface swamp waters charged with azo-silico-humic acids and sulphuric acid derived from marcasite and pyrites; but in the light of recent investigations, there is no doubt that exchange reactions have played an important part in the underground activation of these deposits.

Despite the importance of fuller's earth from the industrial and the theoretical points of view, the ideas expressed in literature as to the mechanism of activation and the clarifying action of fuller's earth and allied clays are diverse in the extreme. Menard and Mellory (Chem. & Met. Eng., 1922, 26, 1074) speak of the mechanical and electrical properties of the fuller's earth as responsible for its bleaching action. The explanation given by Benedict (J. Oil & Fat Ind., 1925, 2, 62) that fuller's earth first promotes oxidation of the colloidal matter and then absorbs the residue, has been questioned by Kutzelnigg (A. Ber., 1930, 63B, 1763) on the ground that oxidising action by a material with a large specific surface is entirely dependent on the adsorbed oxygen and would not therefore, account for the difference of behaviour between fuller's earth and other adsorbents such as charcoal. Amongst those supporting adsorption, there is no unanimity regarding the nature of adsorption and the precise laws governing it. Thus, according to Sloan (Sou. Ca. Geol. Survey, 1904, 59–61), removal of colouring matter is simply mechanical, entangling of the suspended colour particles, while Kobayashi and Yamamoto (J. Soc. Chem. Ind. Japan, 1930, 33, 428) find that adsorption proceeds quantitatively according to the Freundlich formula. Haseman (J. Phys. Chem., 1929, 33, 1514), on the other hand, discredits any explanation based on adsorption; but attributes the bleaching power of the earth to the solid pectoid disilicic acid and its anhydride present in the earth, which are supposed to precipitate the colour-compounds.

The diversity of views can be partly attributed to the fact that fuller's earth varies greatly in its properties and no two deposits seem to be exactly alike. It is possible, nevertheless, to classify the theories which have been put forward to explain the activation and bleaching properties of the earth into three main groups, viz., (1) theories giving prominence to chemical composition of the earth, (2) theories of adsorption, and (3) the recently suggested theory of the zeolitic nature of fuller's earth, based on its structural composition. While adsorption may play an important part in bleaching action, what is responsible for activation as well as clarification by these earths, is their behaviour as hydrogen zeolite as shown by us (Kulkarni and Jatkar, Current Science, 1936, 5, 18).
CHEMICAL COMPOSITION.

Porter's (U. S. Geol. Survey Bull., 1907, No. 315, 268) suggestion that there might exist a well-defined relationship between the rational composition of these earths and the class of colouring matters which a given earth removes most efficiently, has brought forth a considerable amount of analytical data on the subject. Minerologically, fuller's earths appear to be mixtures, some resembling Kaolinite $\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot2\text{H}_2\text{O}$ and may, according to Breithaupt (1841), be supposed to contain smectite, $\text{Al}_2\text{O}_3\cdot7\text{SiO}_2\cdot12\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3\cdot7\text{SiO}_2\cdot6\text{H}_2\text{O}$ as the primary constituents. The first analysis was made by T. Bergman (Stockholm 1780). Analytical values have been subsequently reported by various authors (Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, 1925, 6, 496). The results range from 44.00–72.00 per cent. $\text{SiO}_2$, 5.00–33.38 $\text{Al}_2\text{O}_3$, 4.89–24.95 $\text{H}_2\text{O}$, 1.26–14.87 $\text{Fe}_2\text{O}_3$, 0.33–7.40 $\text{CaO}$, 0.43–4.35 $\text{MgO}$, alkalies 0.45–5.00 with small amounts of organic matter, $\text{SO}_3$, $\text{P}_2\text{O}_5$ and $\text{TiO}_2$. The chemical composition thus varies widely and is in fact no guide to the commercial value of the material. The variations sometimes are so great that analysis alone does not determine whether a particular clay is to be classed as fuller's earth. However, a low silica-alumina ratio and high water-content are admitted by many, although the significance of these characteristics of fuller's earth in activation and clarification is interpreted differently. Both Ries (Ann. Rep. U.S. Geol. Sur., 1896, 17, 880) and Porter (loc. cit.) consider a series of hydrous aluminium silicates as the base of the fuller's earth but the latter author doubts if the bleaching property is entirely due to this. Little significance is attached to the silica-alumina ratio, except that it controls the plasticity of the material (below 3 for non-plastic and above 6 for plastic) (Joseph and Hancock, J. Chem. Soc., 1924, 125, 188), but hydrated silica is considered to be essential for conferring the bleaching properties. Treatment with acids is believed to increase the hydration by converting the silicates into the various hydrosilicic acids which react with the nitrogen compounds of the colouring matter. The presence of such silicic acids is denied by Eckart (Chem. Zentor, 1927, 1, 2615) who does not find free silicic acids in the waste liquors from the treated fuller's earth, while Welds (Z. Angew. Chem., 1927, 40, 7982) attributes the increased activity of the treated earth to the solution of a part of the alumina and iron oxide, principally the former, resulting in a highly porous mass with an extensive surface. It is not, however, made clear why the increased activity consequent on treatment with acid should be so pronounced in the case of fuller's earth and be absent in ordinary clays.
The large surface offered by fuller's earth and its action in removing colours and dyes from oils and liquors brought forth the obvious suggestion that adsorption ought to explain clarifying properties as in the case of adsorbents like charcoal (loc. cit.). The subject has been discussed by Herr (Fuller's Earth, Mineral Resources Bureau, London, 1924), Gilpin (Amer. Chem. Jour., 1910, 44, 251), Gurvitsch (Jour. Russ. Phys. Chem. Soc., 1915, 47, 827), Wessen (Min. Eng. Journ., 1912, 37, 667), Richert (Journ. Eng. Chem., 1917, 9, 599), Vollerston (Cotton Oil Press, 1919, 2, 37) and others. Much stress appears to be laid on the fact that adsorption by fuller's earth follows the Freundlich isotherm. As pointed out by Fisher (Trans. Far. Soc., 1922, 17-11, 310) the Freundlich equation is purely an empirical one and by altering the constants involved a series of curves can be obtained which will fit nearly any set of experimental data with the desired accuracy.

Adsorption in fuller's earth can arise mainly on account of two factors: (1) colloidal nature (neutralisation of charge) and (2) porosity (capillary action). Fuller's earth, containing particles of all grades, must necessarily contain a certain proportion of colloidal matter. Our experiments on deflocculation with different earths, however, show that the portion of fuller's earth is generally very small and in the case of coarse-grained earths, insignificant. Two different earths having the same decolourising efficiency have been found to have different degrees of deflocculation. Furthermore, as Haseman (loc. cit.) has pointed out, it is possible to decrease the proportion of colloidal matter in any particular earth and yet retain its bleaching power intact. The assumption that clarification is solely due to the neutralisation of the electric charges contained in this small proportion of the colloidal matter is untenable. In the first place, the amount of matter removed, is much greater than can be accounted for in this way; secondly, in non-aqueous media such as oil, the colouring matter and dissolved dyestuffs are not electrically charged. Benke (Sorechsaal, 1920, 53, 490) mentions that in aqueous media one gram of kaolin removes 0.0169 gm. of copper oxide from a solution of 4% copper sulphate, 0.077 gm. of ammonia from ammonium chloride, 0.373 gm. of barium from barium chloride and 0.075 gm. of aluminium from aluminium sulphate from N/10 solutions. Removal of such large quantities even by kaolin (which generally contains a greater proportion of colloidal matter than fuller's earth) cannot be explained without assuming chemical actions. Our deflocculation experiments further show that activation does not change the amount of colloidal matter, for the degree of deflocculation remains practically the same before as after activation.
Nor can adsorption be explained on the ground of porosity, although in the case of the zeolitic structures it can afford surplus space for the reacting constituents and an extensive area for the exchange reactions. Activated bentonite, halloysite and illmanite have greater specific gravity and less porosity than fuller's earth, but show greater bleaching power in lubricating oils. If fuller's earth is fused with sodium carbonate, the silicon and aluminium contents separated and reprecipitated with acid under suitable conditions, the product obtained gives a better bleach than the original earth, although less porous.

Adsorption as such, either selective or general, therefore seems to be of little significance in the reactions of these earths except in cases where the earth is extremely finely divided and contains an enormous amount of colloidal matter.

ZEOLITE THEORY.

Investigations on the acidity and base-exchange phenomena in soils have now definitely established the zeolite nature of soils. The idea can be profitably borrowed for application to fuller's earth to explain its activation and clarifying properties. As early as in 1907 Parsons (Jour. Amer. Chem. Soc., 1907, 19, 598; U. S. Bureau of Mines Bull., 1913, 71) pointed out that the American earths are almost generally very acid in reaction as tested by the regular methods used for soils, but still they contain no free acid. Ries (Clays, their Occurrence, Properties and Uses, 1914, 518) also mentions that acidity of fuller's earth is a direct measure of its absorptive capacity for many substances. More recently, Whitney (Bogue: Colloidal Behaviour, McGraw Hill, 1924, 2, 468) in discussing the colloid chemistry of soils has suggested that zeolite-like compounds might account for certain reactions that cannot be explained on the basis of surface phenomena.

It is well known that when a mixture of earth (containing no free acid or alkali) and water is filtered, the filtrate appears to be quite neutral to such indicators as phenolphthalein but if a mixture of the earth and a suitable salt solution is similarly treated, the clear filtrate will be acid to these indicators. This appears to be a characteristic of all the fuller's earths we have examined and the property becomes more pronounced if the earth is previously treated with acids. This apparent acidity without the presence of any free acid, its direct relation to the absorptive power of the earth and an increase in that power by acid treatment can be correlated by postulating that fuller's earth is mainly composed of hydrogen zeolites and that the zeolitic property increases by treatment with acids. The clarifying action is primarily due to reaction between the exchangeable hydrogen and
the colouring matter resulting in compounds which are either colourless or get precipitated and removed along with the earth during filtration (cf. Kulkarni and Jatkar, loc. cit.).

A strong support to the above postulate is obtained from the works of W. and D. Asch (Silicates in Chemistry and Commerce, Constable and Co., London, 1913) who have discussed at length the structure and constitution of the zeolitic alumino-silicates in the light of their hexite-pentite theory of the silicates. On the basis of this theory, fuller's earth can be regarded as consisting of a mixture of salts including normal, basic, acid or mixed salts, which, in the simplest form can have the following structures wherein \( \text{Si} \) stands for \( 6\text{SiO}_2 \) and \( \text{Al} \) stands for \( 3\text{Al}_2\text{O}_3 \).

![Diagram of zeolite structures]

Clarke's zeolites are represented on the basis of this theory, as follows:

Clarke's formula for Laumontite multiplied by \( 3/2 \) gives

\[
6\text{H}_2\text{O} \cdot 3\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 12\text{SiO}_2 \cdot 6\text{H}_2\text{O}
\]

![Clarke's formula for Laumontite]

where \( C_6 = \frac{1}{2} \text{ Ca} \).
similarly Clarke's formula for Hydronephelite multiplied by 4 gives
\[4Na_2O \cdot 2H_2O \cdot 6Al_2O_3 \cdot 12SiO_2 \cdot 12H_2O\]

The properties of fuller's earth can be accounted for on the basis that the earth is primarily a mixture of zeolite salts of structures similar to those given above. It will be observed that such a mixture is capable of considerable irregularity and the atomic groupings, while retaining their zeolitic structure, are capable of great variation depending on the valencies of the atoms forming them and the geological history of the deposit in which they occur. Neither microscopic examination nor mere analysis will therefore distinguish fuller's earth from other clays.

Acid earths can be considered as containing an excess of acid salts, and basic earths as containing a larger proportion of the basic salts. These structures also explain very satisfactorily the activation of the earth by treatment with acids. The side-atoms about the silicon and aluminium hexagons are capable of considerable reactivity and exchangeability. Activation by acid then simply consists in loading the structural molecule with replaceable hydrogen atoms to the extent consistent with the stability of the structure.

A deeper insight into these structures is obtained from the crystallographic studies of the silicates by Bragg (Trans. Far. Soc., 1929, 25, 291). His investigations reveal that silicates are made up of ions which act as impregnable spheres with characteristic diameters. The small but highly charged Si and Al ions are surrounded by four or six oxygen ions forming tetrahedrons or octahedrons, of which the aluminium silicates are considered to be built up. These may be in either closed or open packing. The nature of packing will no doubt play an important part in the reactivity of the crystals. The open packed systems (which are obtained in zeolites) present the pattern of alternating aluminium and silicon tetrahedra with surplus space for the "wandering constituents" (Jaeger, Trans. Far. Soc., 1929, 25, 320). They can thus be considered to have more porosity (in the sense mentioned by Welds, loc. cit.) than alumina or silica, which are systems with closed packing and do not permit ions to enter the crystal on account of the architectural arrangement of the oxygen atoms. This distinguishes fuller's earth which is mainly composed of open-packed zeolitic structures from the ordinary clays in which systems with closed packing predominate.
It is also interesting to consider the water-content of these earths, the effect of heat thereon and the consequent changes in the properties of these bodies. Water may be present in these bodies either as "water of crystallization," or "water of constitution," the latter being acid or base water. The acid water may be of various kinds: part of the hydroxyl groups may be united to aluminium hexite or pentite, the remainder to the silicon hexite or pentite, or the hydroxyl group may be united through another metallic radicle like Na, Ca or NH₄, forming basic water. As Serle (The Chemistry and Physics of Clays, 1924, 336) has pointed out, the zeolitic structures are characterised as having large number of (OH) and (H) groups which may be considered to form the water of constitution in addition to water of crystallization. This explains the high water content of fuller's earth and the allied clays. Welds (loc. cit.) has given special attention to the action of heat on fuller's earth at various temperatures and has tried to correlate the loss of water and the amount of soluble aluminium iron oxides in samples of earths heated for definite periods at temperatures up to 1000°C. His observations are consistent with the zeolitic conception. The progressive loss of water is usually interpreted as strongly supporting the colloidal nature of the earth, but as Welds' results show this loss is not so regularly progressive as is found, for instance, in the case of gels. It must also be remembered that the earth consists of a number of hydrated crystals, about the vapour pressure of which, no systematic study has yet been made. The water-content of earths and clays is an important problem in soil-chemistry and its study is bound to throw further light on the structures of these earths. For the present we can safely assume that in the case of zeolitic structures, the molecules by heat-treatment will lose the (OH) groups together with the reactive (H) groups and thus the reactivity of the earth which depends on the more reactive (H) groups will suffer. With prolonged heating, the molecules may ultimately break down resulting in a loss of water and an increase in the oxide-content.

A detailed study of the decolourising action and activation of the fuller's earth by acids based on the zeolitic theory will be published in Part II.

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