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**REACTION OF LIME WITH
FERRIC OXIDE**

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IT has recently been suggested that the adsorption of lime by fired kaolin and kaolinitic clay, in presence of water, may be considered to be a semiconductor surface reaction¹. It was also found that the adsorption of lime decreased with the increase in the electrical conductivity of these materials^{1,2}. In this article the reaction between lime and $\alpha\text{Fe}_2\text{O}_3$ (obtained from fired laterite) in the presence of water is considered. The problem arose during a study of the puzzolanic activity of laterite.

At low electrical conductivity of Fe_2O_3 it reacted very little with lime. At high conductivity, reactivity increased but remained constant over a wide range of conductivity, that is, saturation in reaction was obtained. On firing laterite with admixture of small quantities of Cr_2O_3 , TiO_2 , ZnO , NiO and CoO the nature of the reaction between Fe_2O_3 thus obtained and lime remained generally unaltered. On firing with Cu_2O , at low values of conductivity, the reactivity increased with the decrease in conductivity and at high conductivity, saturation was obtained.

The parallel change in reactivity with conductivity, when considered with the fact that Fe_2O_3 is a 'p' type semiconductor in an oxidizing atmosphere, indicates that the reaction between lime and Fe_2O_3 in presence of water is a 'p' type reaction on a 'p' type semiconductor. The opposite behaviour in Fe_2O_3 obtained when laterite is fired with Cu_2O indicates that Fe_2O_3 may have changed into an 'n' type semiconductor and the reaction is a 'p' type reaction on a 'n' type semiconductor.

A quantity of laterite was powdered, sieved through B.S. 200 mesh and fraction passing through was thoroughly mixed and the samples from it were analysed chemically and by X-ray and differential thermal analysis.

About 200 g of the sample was drawn from this lot for each experiment and was fired in ordinary atmosphere, as such or with admixture of 1 per cent by weight of Cr_2O_3 , TiO_2 , ZnO , NiO , Cu_2O and CoO . Firing temperatures for natural laterite were 350°, 550°, 675°, 800° and 950° C and those with oxides were 350°, 550°, 675° and 800° C. The firing period was 4 h in each case. The mass obtained on firing was examined visually and under a microscope. No sintering could be detected which meant

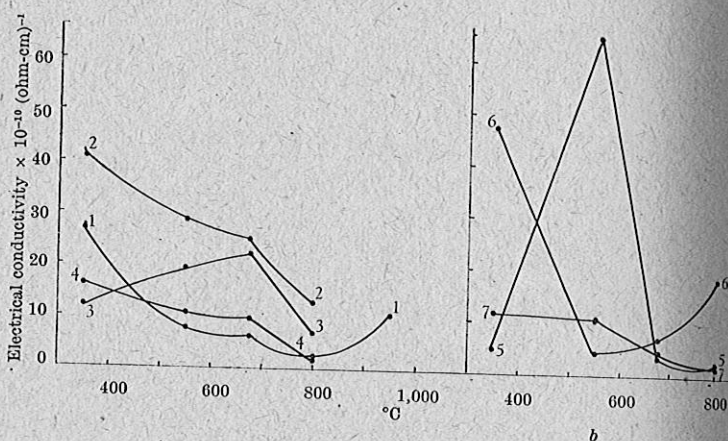


Fig. 1. Variation of room temperature electric conductivity of ferric oxide with firing temperature. *a*, Curve 1, Fe₂O₃ from fired laterite; curves 2, 3, 4 from laterite fired with admixture of Cr₂O₃, TiO₂ and ZnO. *b*, Curves 5, 6, 7, Fe₂O₃ from laterite fired with NiO, Cu₂O and CoO

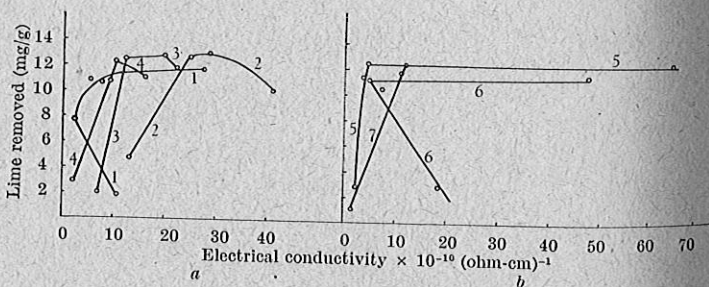


Fig. 2. Variation of lime reactivity of fired ferric oxide with room temperature electrical conductivity. *a*, Curve 1, Fe₂O₃ from fired laterite; curves 2, 3, 4, Fe₂O₃ from laterite fired with Cr₂O₃, TiO₂ and ZnO. *b*, curves 5, 6, 7, Fe₂O₃ from laterite fired with NiO, Cu₂O, CoO

that the specific surface area remained unchanged. The fired mass was washed clean of colloidal suspensions, dried at 110° C for 24 h and sieved through B.S. 300 mesh. A large portion of the sieved mass had the linear size below the 'screening length' (10^{-4} cm).

The amount of lime removed by the material from a saturated lime solution, at constant temperature $35 \pm 0.5^\circ$ C and in an atmosphere free of carbon dioxide, at intervals of 1 min was measured by the method described earlier². Adsorption was rapid initially and the process continued at a slow rate for a long time and equilibrium conditions was not obtained even after 48 h but a near equilibrium condition was obtained after 5 min. Lime removed by 1 g of the material during the first 5 min was taken as a measure of its reactivity.

For electrical conductivity measurements the samples were made into tablets using a 20-mm cylindrical mould and plunger. 3 g of samples was placed in the mould and compressed in a hand-operated hydraulic press at a total pressure of 1,000 lb. (Electrical conductivity was found to vary slightly with pressure.) The tablets, taken out of the mould, were coated on the flat ends with a dilute suspension of aquadag in alcohol. These were then dried at 110° C for 24 h and cooled to room temperature over fused calcium chloride and soda lime.

Resistance of the tablets was measured at ordinary temperatures and in ordinary atmosphere with a General Radio megohm bridge by placing the tablets between two flat platinum electrodes under a slight pressure. In some of the specimens resistance was found to increase slowly during measurements; and in such cases resistance at the establishment of contact was taken. There was also a slight change in conductivity with temperature but this was neglected in the present experiments.

Chemical analysis of the laterite sample is (per cent): loss on ignition 14.09, silica and insolubles 30.87, iron (Fe_2O_3) 35.04, aluminium (Al_2O_3) 18.12, calcium (CaO) 0.56, magnesium (MgO) 0.91 and alkalis nil.

X-ray diffraction pattern of the powdered laterite samples shows the presence of goethite, kaolinite and quartz. The differential thermal analysis curve shows endothermic peaks at 125°, 330° and 565° C and an exothermic peak at 940° C. These are identified as due to goethite, kaolinite and gibbsite.

Specific electrical conductivity of the samples of the natural laterite powder passing B.S. 300 mesh, washed, dried and tableted, was found to be order of 9×10^{-9} (ohm-cm)⁻¹ at ordinary temperature. Its lime reactivity at $35 \pm 0.5^\circ \text{C}$ was 8.18 mg/g.

X-ray powder patterns of the fired samples used for lime and resistance measurements show mainly the pattern of $\alpha\text{Fe}_2\text{O}_3$. Variation of (room temperature) electrical conductivity of Fe_2O_3 with firing temperature is shown in Fig. 1a. Up to 800° C conductivity generally decreases with the firing temperature with a slight hump at 675° C. A rise in conductivity is observed in the samples fired at 950° C.

Curves 2, 4, 5 and 7 (Fig. 1a and b) show variation in the electrical conductivity with firing temperature of the laterite samples with admixture of Cr_2O_3 , ZnO, NiO and CoO. When fired with Cr_2O_3 , the room temperature conductivity of Fe_2O_3 is higher (at the corresponding temperature) than the product obtained by firing laterite alone. Decrease of conductivity is, however, maintained. With ZnO, conductivity at 350° C is lower, at 550° and 675° higher and at 800° C of the same order as that of the ordinary laterite fired at the corresponding temperatures.

With NiO, when fired at 350°, 675° and 800° C, the conductivities are much lower and show a gradual decrease but when fired at 550° C conductivity has a high value (6.5×10^{-9} (ohm-cm)⁻¹). With CoO (curve 7) the conductivities are low but these also decrease with firing temperature. Curve 3 (Fig. 1a) shows the effect of TiO₂. Conductivity increases up to 675° C and falls to a low value at 800° C. Curve 6 (Fig. 1b) shows effect of Cu₂O. There is a large increase in conductivity when fired at 350° C; at 550° C it decreases but again increases at 675° C and 800° C. There are humps at 675° C in the conductivity-firing temperature curves for natural laterite as well as for laterite fired with 'n' type oxides (Fig. 1a). When fired with 'p' type oxides the hump has shifted to a lower temperature (550° C).

Curve 1 (Fig. 2a) shows the variation of lime reactivity with (room temp.) electrical conductivity of Fe₂O₃ obtained from laterite fired without admixture. At low values of conductivity, reactivity increases with conductivity but at high values the reactivity tends to a saturation value. There is a reversal in the specimen fired at 950° C. Here conductivity is increased but reactivity decreases.

Curves 2, 3 and 4 (Fig. 2a) show the variation of reactivity with conductivity of the samples obtained after firing with Cr₂O₃, TiO₂ and ZnO. These are similar to curve 1 except for a slight decrease in reactivity at high conductivity which might indicate desorption. The nature of the curves from samples fired with NiO and CoO (Fig. 2b, curves 5 and 7) is similar to curve 1. Curve 6 is for samples heated with Cu₂O. At high conductivity saturation is obtained but at low values the reactivity decreases with conductivity.

Specific electrical conductivity of pure Fe₂O₃ is of the order of 10^{-13} (ohm-cm)⁻¹. Higher conductivity obtained in these experiments may be the result of impurities present.

Fe₂O₃ can be either a 'n' type or a 'p' type semiconductor depending on the valence state of the cation. Oxidation changes pure Fe₂O₃ into a 'p' type semiconductor. In these experiments Fe₂O₃ has been produced by heating laterite in an oxidizing atmosphere. A possibility is that the Fe₂O₃ used is a 'p' type oxide. Further, on heating with Cr₂O₃, TiO₂, ZnO and Cu₂O (lower valency cations) an increase in conductivity is observed at corresponding firing temperatures in almost all cases. With higher valency cations there is a decrease in conductivity. These facts confirm that Fe₂O₃ used here is a 'p' type semiconductor.

The decrease in conductivity of Fe₂O₃ with temperature may be due to annihilation of 'holes' by combination with electrons provided by Al₂O₃ (from the decomposition of gibbsite and entering into a solid solution in Fe₂O₃). The fall in conductivity (as well as of reactivity) at 800° C may be due to combination of 'holes' with electrons from

enhanced quantity of Al_2O_3 entering into a solid solution with Fe_2O_3 . This is possible because of the breakdown of kaolin structure into Al_2O_3 and SiO_2 . (There is also a large change in the electrical resistivity of kaolin between temperatures $700^\circ\text{--}800^\circ\text{C}$) (ref. 3). Increase in conductivity when fired at 950°C may be due to more Al_2O_3 entering into solid solution.

Introduction of donor impurities into a semiconductor crystal raises the Fermi level of the crystal towards its conduction band. Under equilibrium conditions, for a 'p' type reaction, a shift of the Fermi level towards the conduction band adversely affects the number of particles involved in a chemisorption process. Thus the observed fall in reactivity with decrease in electrical conductivity for Fe_2O_3 obtained from fired laterite (Fe_2O_3 was being fired in presence of Al_2O_3) may be explained, if it is assumed that the reaction is a 'p' type reaction on a 'p' type semiconductor. Effect of admixture of 'n' type oxides as Cr_2O_3 , TiO_2 and ZnO can be explained in a similar way.

In the sample heated at 950°C the reaction is probably 'p' type on a 'n' type semiconductor.

On heating with Cu_2O in the range $550^\circ\text{--}800^\circ\text{C}$ reactivity varies with conductivity in opposite direction. This may happen if the reaction is assumed to be a 'p' type reaction on a 'n' type semiconductor. Fe_2O_3 may be changed into a 'n' type semiconductor through Fe^{3+} changing to Fe^{2+} through reduction by Cu .

NiO and CoO have scarcely affected the reactivity of Fe_2O_3 in the way they are expected to do.

The humps at 675°C in the conductivity-firing temperature curves (Fig. 1a) may be due to change of Fe_2O_3 from its antiferromagnetic state to a paramagnetic one when fired at that temperature. ($\sim 675^\circ\text{C}$ is the Néel temperature for Fe_2O_3 .) If this is so, then the chemical reactivity of Fe_2O_3 becomes connected with its magnetic property through its semiconducting property and one expects that such a connexion should exist. The explanation of some of the observed results would then need some modification.

The reaction between Fe_2O_3 (obtained from fired laterite) and lime in the presence of water is a semiconductor surface reaction. The reaction type is a 'p' type reaction on a 'p' type semiconductor. Fe_2O_3 may be changed into a 'n' type semiconductor by heating with Cu_2O above 550°C or with active Al_2O_3 above 800°C .

These conclusions need verification with pure Fe_2O_3 and experiments with this in view are in hand.

This article is submitted with the permission of the Director, Central Building Research Institute, Roorkee, India.

¹ Chatterji, A. K., *Nature*, 192, 1180 (1961).

² Chatterji, A. K., Phatak, T. C., and Dhariyal, K. D., *J. Sci. Indust. Res. (India)*, 19B, 493 (1960).

³ Chatterji, A. K., Murthy, T. V. S., and Patwardhan, N. K. (unpublished results).