# EFFECT OF CATALYTIC AGENTS ON THE PHASE-TRANSFORMATION OF GÖTHITE

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## INTRODUCTION

Recently we (1955) have studied the complete phase-transformations of the monohydrated iron-oxide minerals, viz. Limonite and Göthite, during thermal treatments. The common faith of the mineralogists that Limonite was amorphous, was proved to be baseless by Posnjack and Merwin (1922). We (1952) have also shown that Limonite is definitely crystalline. Göthite and Limonite have the identical molecular structures but their physical appearances and properties are quite different from each other. The complete chemical analysis also gives different amounts of iron-oxide and water in different samples of Limonite and Göthite. But their molecular structures being similar, they must have the same molecular formula. But so far the earlier workers depended on the chemical analysis alone, they could not determine the exact percentage of adsorbed water in Limonite and Göthite. Moreover, the common impurities present in those minerals were $SiO_2$, $TiO_2$, $MnO_2$, etc. It is likely that these impurities and the adsorbed water enter the pores and capillaries of those minerals thereby taking no part in the structural distribution. In order to determine the amount of adsorbed water in those minerals, we had carried out differential thermal, thermal and X-ray analysis of Limonite and Göthite. It was seen that with the rise of temperature both Limonite and Göthite lost some percentage of water, which was definitely due to the expulsion of water from the minerals. X-ray analysis showed that though Göthite and Limonite lost a certain percentage of water during heating, the original structure did not break down up to a certain temperature, which was different for Limonite and Göthite. The transition temperature for Limonite was 210°C. and for Göthite it was 250°C. The only explanation for this variation in the transition temperature may be the different amounts of adsorbed water and impurities present in the minerals and also the different particle sizes of Limonite and Göthite. But a look at Table I would show that the amount of adsorbed water and impurities in different samples of Limonite and Göthite are different.

TABLE I

*The actual percentage composition of Göthite and Limonite*

| Samples | % of $Fe_2O_3$ | % of impurities $SiO_2$ | Water | |
|---|---|---|---|---|
| | | | Crystalline | Adsorbed |
| Göthite (Alabama) .. | 86·1 | .. | 9·7 | 4·0 |
| Limonite (Alabama) .. | 81·9 | 2·78 | 9·32 | 6·0 |
| Limonite (Jubbulpur) .. | 84·44 | 5·78 | 9·68 | 0·1 |

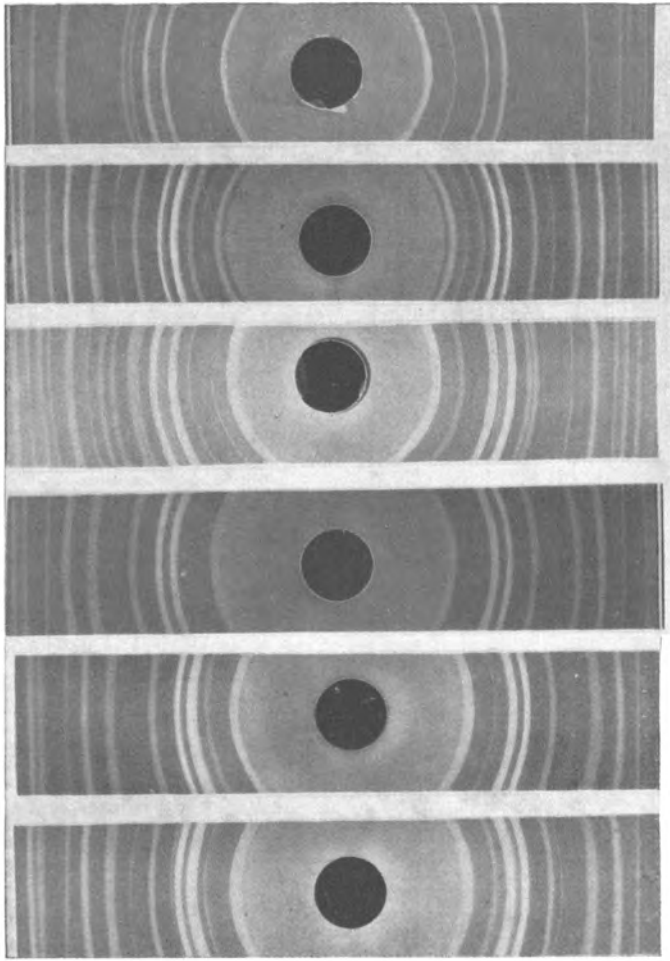


FIG. 1 (A). Powder diffraction patterns of Göthite and amorphous silica heated at different temperatures.
Silica added (*a*) 0·5%, (*b*) 0·5%, (*c*) 1·5%, (*d*) 1·5%, (*e*) 2·0%, (*f*) 2·5%.

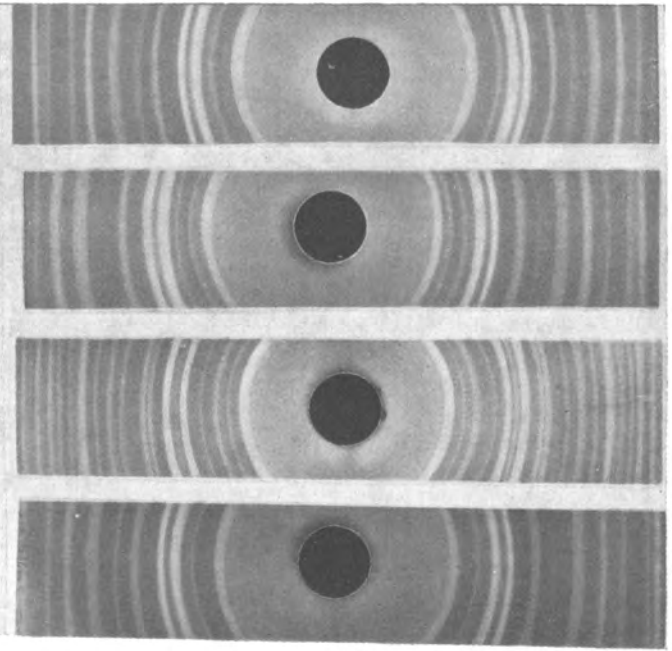


FIG. 1 (B). Powder diffraction patterns of Göthite and crystalline silica heated at different temperatures.
Silica added (*a*) 1·5%, (*b*) 2·0%, (*c*) 2·5%, (*d*) 2·5%.

Had the water (adsorbed) been responsible for the variation of transition temperature we would get, for different samples of Limonite, different transition temperature. But the transition temperature for all samples of Limonite was found to be 210°C. So we could easily discard the effect of the adsorbed water on the phase-transformation of Limonite. Moreover, the different particle sizes and amount of impurities in those minerals, may have some catalytic influence on the phase-transformation of those minerals. It was for this reason, i.e. to see the rôle played by the silica on the phase-transformation of Göthite, the present work was taken in hand.

## Experimental

Göthite was crushed to fine powder in an agate mortar. Known weight of silica was added to a known weight of powdered Göthite. This was then heated in a furnace at a particular temperature for at least twenty-four hours. Different samples, having different percentages of silica and Göthite, were thus prepared. All these samples were then heated at various temperatures. Silica was added both in amorphous and crystalline forms. X-ray powder diffraction photographs of all these samples, having different thermal history, were taken in cylindrical camera, using Fe $K$-radiations from a Hadding-tube, run at a voltage of 40 kV with a tube current of 10 ma. The exposure time of each photograph was at least eight hours. The following table (Table II) and figures (Plate XV, Figs. 1 (A) and 1 (B)) will give the experimental results.

Table II

(A) *Effect of amorphous silica on Göthite*

| % of silica added | Temperature to which the mixture was heated | Structure after thermal treatment |
|---|---|---|
| 0·5 | 230°C. | Same as Göthite |
| 0·5 | 235°C. | Same as $Fe_2O_3$ |
| 1·5 | 225°C. | Same as Göthite |
| 1·5 | 230°C. | Same as $Fe_2O_3$ |
| 2·0 | 220°C. | Same as $Fe_2O_3$ |
| 2·5 | 210°C. | Same as $Fe_2O_3$ |

(B) *Effect of quartz on Göthite*

| % of quartz added | Temperature to which the mixture was heated | Structure after thermal treatment |
|---|---|---|
| 1·5 | 225°C. | Same as $Fe_2O_3$ |
| 2·0 | 220°C. | Same as $Fe_2O_3$ |
| 2·5 | 200°C. | Same as Göthite |
| 2·5 | 210°C. | Same as $Fe_2O_3$ |

## Discussions

The main object of the present work was to see whether silica added to Göthite could form any chemical compound with Göthite when heated up to high temperatures or they simply behaved as a catalytic agent so as to hasten the reaction during which Göthite was being transformed into $Fe_2O_3$. That silica could not form any chemical compounds with Göthité is quite evident from the fact that we could not obtain any

diffraction patterns which were quite different either from that of Göthite or of $Fe_2O_3$. Had it formed any definite chemical compound we could have found a different diffraction pattern.

Moreover, it has been stated earlier that the transition temperature for Göthite is 250°C. But we, in the present investigation, have found that this transition can be made to take place at lower temperatures by gradually increasing the amount of silica added. It is known that the presence of any catalytic agent can cause a change in the transition phenomenon. It is likely that in this case the presence of silica has a catalytic influence on the phase-transformation of Göthite. But in all the pictures we have not found any line or band due to the presence of silica in the mixture with Göthite. The cause for this was that the percentage of silica added was too small to give any line or band in the diffraction pattern.

Actually it was found that with the increment of the amount of silica the transition temperature changes. With 0·5% of silica the transition temperature was found to be shifted from 250°C. to 235°C. (Table III). With 1·5% of silica it was 230°C., when the transition temperature came down to 210°C. at a concentration of 2·5% of silica in the mixture. By increasing the amount of silica, it was found not possible to lower down the transition temperature below 210°C. Similar was the case when amorphous silica was replaced by crystalline quartz. Thus it was seen that the saturation limit to cause any change in the transition temperature of Göthite was reached when the presence of silica in the mixture was 2·5%.

TABLE III

*Bragg angles and spacings of the diffraction pattern of the mixture of Göthite and silica (0·5%) heated to 235°C.*

| Bragg angle | Intensity | Spacings | Spacings of $Fe_2O_3$ by Hanwalt, Rinn and Fravel |
|---|---|---|---|
| 21°5′ | s | 2·698 | 2·69 |
| 22°43′ | s | 2·512 | 2·51 |
| 26°5′ | m | 2·207 | 2·20 |
| 30°41′ | w | 1·847 | 1·84 |
| 34°55′ | m | 1·695 | 1·69 |
| 40°55′ | m | 1·452 | 1·452 |

The spacings and Bragg angles of all the other patterns of the mixture of silica and Göthite (heat treated) where Göthite is said to be changed are similar to the above.

From this study, we can also account for the different type of transformation in Göthite and Limonite, both having the similar molecular structure. Chemical analysis of Limonite (Table I) shows that in the Jubbulpur sample, the amount of silica present was 5·78% and 2·78% in the Alabama sample. It has been already seen that the presence of 2·5% of silica in Göthite was sufficient to change the transition temperature to 210°C. Thus it is seen that the amount of silica present in Limonite is quite greater than the limiting amount of silica necessary to transform Göthite to $Fe_2O_3$ at 210°C. It is also likely that the amount of silica present in Limonite is responsible for its different physical properties and appearances from those of Göthite, though Limonite has the same structure as that of Göthite.

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## Abstract

During the phase-transformation study of monohydrated iron-oxide minerals, Limonite and Göthite, on thermal treatments, it was found that though the two minerals have identical structures, the transition temperatures for Limonite and Göthite are quite different. The cause for this difference was attributed to the different amounts of impurities present in the minerals. In the present investigation the impurities, which were present in Limonite, were added to powdered Göthite by different amounts and their effects on the phase-transformation of Göthite during thermal treatments were studied by X-ray diffraction method. It was found that, with the increasing amount of the impurities added, the transition temperature was also lowered. But up to a certain amount of impurities added, the transition temperature came down as low as 210°C. from 250°C. in the case of Göthite. After that further addition of impurities did not cause any change in the transition temperature. From this study the cause for Limonite having a lower transition temperature was also well established.

## References

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