

# Value addition to unutilized iron oxide generated from spent acid in chloride route TiO<sub>2</sub> manufacturing process

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**Abstract** - The iron oxide generated as a result of the acid regeneration process of spent acid produced during benelite ilmenite beneficiation is high in chlorides and hence does not find any potential application. A method is proposed for reducing the chloride content of iron oxide thus produced, to significant levels. The composition of iron oxide is determined by analytical and instrumental techniques. The sample is characterized by X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Calcinations at high temperature has found to reduce the chloride content enabling the iron oxide to be possibly used in a number of applications without the issue of any environmental emissions and damage of equipments/vessels. A system is also proposed to execute the findings of the investigative work.

**Key Words:** Iron Oxide, Calcination, Chloride, Spent Acid

## 1. INTRODUCTION

The process of commercial production of TiO<sub>2</sub> from titaniferous ores by the chloride route includes a combination of operational steps to economically produce high quality synthetic rutile [1 - 8]. In the Benelite process [2] for purifying titaniferous ores, the ores after being reduced to the divalent state is subsequently subjected to leaching operation for dissolution of undesired non-titaniferous values in the ore. The management of the spent liquor generated during the above process represents a major environmental issue although many studies are reported for the recovery of valuables from it [9 - 15]. Pyro hydrolysis of the spent liquor for recovery of

hydrochloric acid [16 - 18] generates an impure iron oxide with no marketable outlets and hence a solid waste results.

The high acidity and chloride content in the iron oxide limits it from being used for a variety of applications. Thus the generation of iron oxide during the hydrochloric acid recovery process poses a big environmental challenge related to stocking of the solid waste. The more recovery and recycling of useful metals from wastes, the less environmental damage that will result from waste disposal.

A survey of literature shows that no papers are available with regard to the value addition or disposal of iron oxide generated during the pyrohydrolysis of spent acid. The iron oxide generated during the acid regeneration process at The Kerala Minerals and Metals Ltd. is stored in lined ponds. Attempts to use this iron oxide as partial substitute to iron ore in steel manufacturing, iron recovery etc., though yielded very encouraging results, have resulted in damage of pellet making machine, erosion of furnace lining etc. due the acidic emissions. The above efforts clearly indicate that this iron oxide cannot be directly used for majority of potential applications without any processing or value addition. Hence it is highly imperative to find a solution to reduce the chloride levels in the iron oxide significantly to enable the same to be used in a variety of applications.

The present paper attempts to develop a process to reduce the chloride content in iron oxide to considerable levels thereby making it a value-added product. Detailed investigations are carried out on the characterization of the processed iron oxide and a system is proposed to execute the process developed.

## 2. METHODS

### 2.1 Materials

Iron oxide (generated as a result of acid regeneration of spent hydrochloric acid resulting from Benelite process) was collected from The Kerala Minerals and Metals Limited.

### 2.2 Analysis

Analysis of total chloride and total iron were performed using standard volumetric analytical techniques. All the trace elements were analyzed using atomic absorption spectrometer (PinnAAcle 900 F, PerkinElmer). The aluminum reduction technique (ASTM test method D1354-76) was employed to analyze the TiO<sub>2</sub> content of the samples.

### 2.3 Characterization

XRD measurements were performed using XRD diffractometer (Rigaku, Miniflex II) operating in Cu K $\alpha$  radiation and investigation on the morphology of the samples was carried out using SEM (Jeol 6390LV) at an accelerating voltage of 30 KV and TEM (Jeol JEM 2100) at an accelerating voltage of 200 KV.

### 2.4 Experimental

The reddish brown coloured iron oxide was subjected to heating at elevated temperature to examine any reduction in the chloride content. These heating experiments were performed over a wide range of elevated temperatures in a muffle furnace.

200 gram of iron oxide were initially air dried and then subjected to heating (calcination) at varying temperatures (100 to 700 °C) in a silica dish placed in the furnace for about 180 minutes each. The heated/calcined samples were cooled and analyzed for the composition and chloride content employing the above-mentioned techniques. The iron oxide before and after calcinations are termed as IOR and IOC respectively for further references.

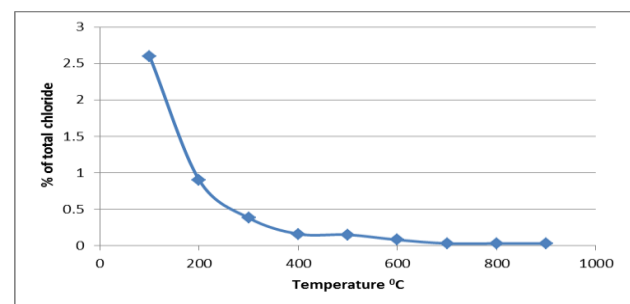
## 3. RESULTS AND DISCUSSION

The typical compositions of iron oxide before and after calcinations are given in Table 1. The chemical/instrumental analysis of IOR indicated the presence of 82.38% Fe<sub>2</sub>O<sub>3</sub>, 8.12% TiO<sub>2</sub>, 1.25% MgO, 0.86% Al<sub>2</sub>O<sub>3</sub>, 0.63% SiO<sub>2</sub> and 2.70% total chlorides. The predominant constituent in both the samples is iron oxide. Oxide constituents of V<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>, and MnO are also found in the sample. It is clearly evident from the above table that the calcination at elevated temperature has diminished the chloride content thereby enriching the iron values in it.

**Table -1:** Typical Compositions of iron oxide before and after calcination at 500 °C

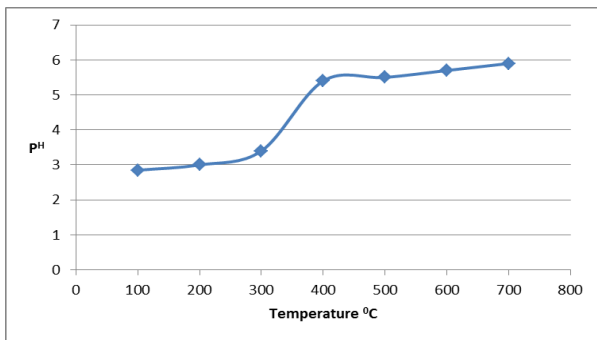
Sl. No	Constituent	Composition (%)	
		Before Calcination	After Calcination
1	Fe <sub>2</sub> O <sub>3</sub>	82.38	86.10
2	TiO <sub>2</sub>	8.12	8.36
3	V <sub>2</sub> O <sub>5</sub>	0.44	0.97
4	Al <sub>2</sub> O <sub>3</sub>	0.86	0.94
5	MnO	0.46	0.52
6	Cr <sub>2</sub> O <sub>3</sub>	0.16	0.2
7	MgO	1.25	1.32
8	SiO <sub>2</sub>	0.63	0.68
9	Total chlorides	2.70	0.15
10	Moisture	2.55	0.34

The profile of chloride content in the samples when subjected to heating at elevated temperatures is depicted in Fig. 1. The total chloride in the sample has been found to decrease with temperature. The volatile chlorides has released off from the iron oxide as seen from the values dropping to around 0.15% for IOC from 2.7% for IOR upon heating the sample at 500 °C which is a significant observation.



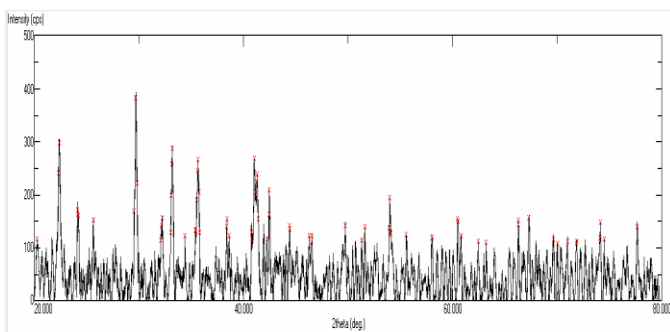
**Fig -1:** Total Chloride in iron oxide as a function of temperature

The paradigm of pH of the iron oxide at elevated temperatures is revealed in Fig. 2. The low pH of IOR indicates escalated levels of acidity. The pH values are found steadily increasing upon increase in temperature as a result of reduction of chloride levels and hence reducing the acidity of iron oxide considerably.

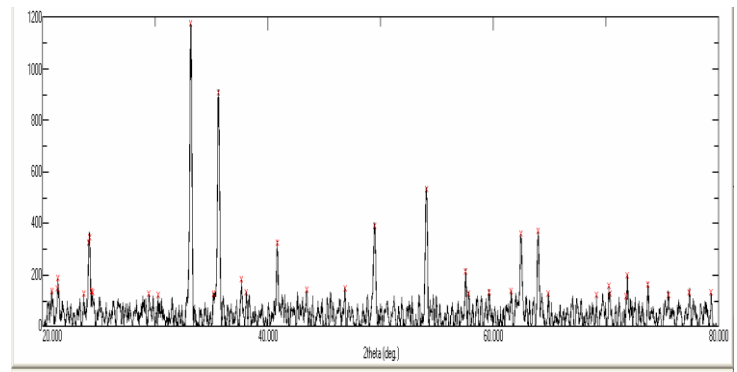


**Fig -2:** Variation in pH of iron oxide against temperature.

The XRD patterns of IOR and IOC samples are shown in Fig. 3a and 3b respectively. IOR sample showed strong peaks at  $2\theta \sim 22.4^\circ$  and  $29.7^\circ$  and weak peaks at  $2\theta \sim 33.1^\circ$  and  $35.6^\circ$  while calcined IOC demonstrated two strong peaks and four weak diffraction peaks at  $2\theta \sim 33.1^\circ$ ,  $35.7^\circ$ ,  $24.1^\circ$ ,  $40.8^\circ$ ,  $49.4^\circ$  and  $54.1^\circ$ . The diffraction peaks appearing at  $2\theta \sim 29.7^\circ$  and  $35.6^\circ$  could be attributed to  $Fe_3O_4$  face-centered cubic structure. No drastic change in the diffraction pattern was observed after calcinations, but when minutely examined the sharpness of diffraction pattern at  $2\theta \sim 35.6^\circ$  was slightly increased to  $35.7^\circ$  possibly due to the increase in crystalline size upon calcination. The peak at  $33.1^\circ$  can be ascribed by hematite phase of  $Fe_2O_3$  [19]. New peaks are found to appear at  $2\theta \sim 24.1^\circ$ ,  $40.8^\circ$ ,  $49.4^\circ$ , and  $54.1^\circ$  and strengthening of the peak at  $2\theta \sim 33.1^\circ$  and  $35.6^\circ$  for the calcined samples. The latter confirms the artifact of  $\alpha-Fe_2O_3$  crystallite. The diffraction peaks centered at  $2\theta \sim 24.1$ ,  $33.1$ ,  $35.6$ ,  $40.8$ ,  $49.4$ , and  $54.1$  may be assigned to hexagonal rhombic  $\alpha-Fe_2O_3$  (hematite) [19]. Hematite is an antiferromagnetic insulator with corundum structure in which  $Fe^{3+}$  ions are octahedrally coordinated by  $O^{2-}$  ions which are organized in hexagonal structure [19]. All the above results suggest in addition to reduction of chloride content, that phase and structure of iron oxide can be tailored and direct transition from  $Fe_3O_4$  (magnetite) to  $\alpha-Fe_2O_3$  (hematite) can be achieved as a result of calcination at elevated temperatures above  $500^\circ C$ . The strong and sharp diffraction peak around  $2\theta \sim 33.1$  was employed to estimate the mean crystalline size of  $\alpha-Fe_2O_3$  using Debye-Scherrer formula and found to be  $\sim 197$  nm.

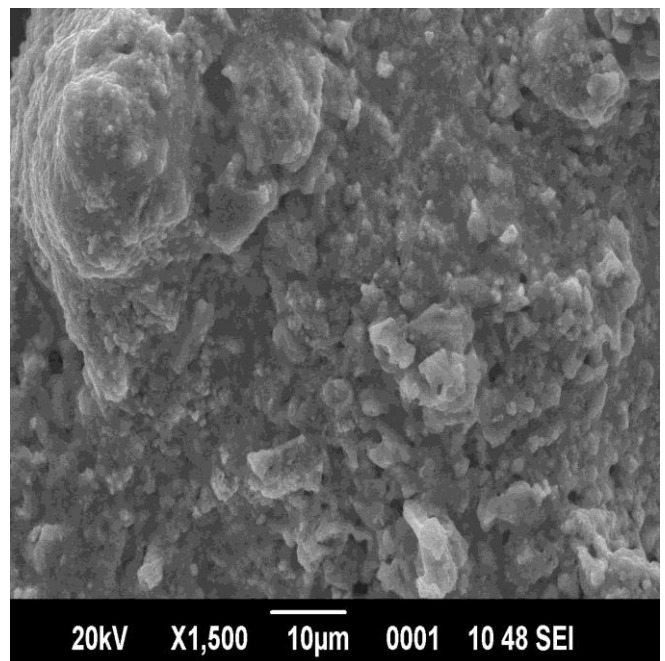


**Fig -3a:** XRD pattern of noncalcined iron oxide.



**Fig -3b:** XRD pattern of Calcined iron oxide

Figs 4a and 4b reveal the morphology of the iron oxide sample (IOC) calcined at  $550^\circ C$  by SEM and TEM observations respectively. In the SEM image, one may clearly observe the particles with irregular shapes and size. The particle size of the calcined samples varied between  $100$  nm to more than  $200$  nm as revealed from TEM which supports the results of XRD. Iron oxide grains are present in different shapes like round, sub-round, lath, prismatic etc and look brittle in nature. Some particles are partially fractured and shattered. The TEM image also exhibits weak aggregation of particles indicating development of super paramagnetic structure.



**Fig -4(a):** SEM image of calcined iron oxide

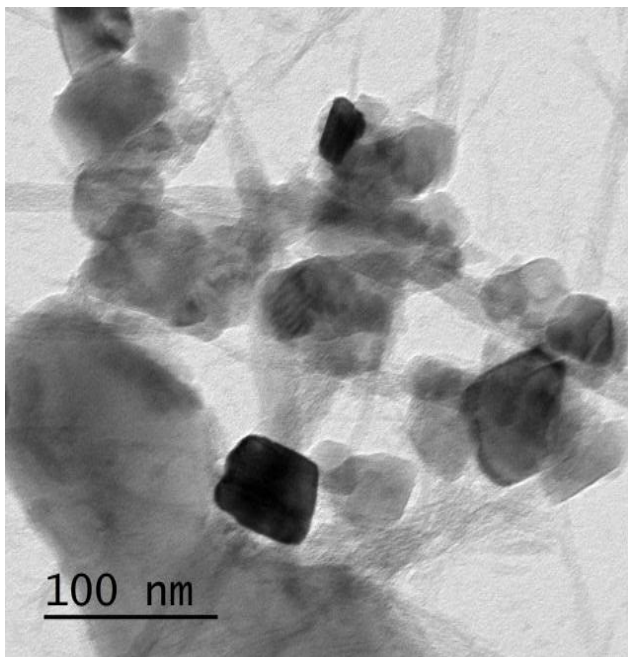


Fig -4(b): TEM image of calcined iron oxide

In the context of the results of above studies, a process is proposed for executing the calcination process for reduction of iron oxide to lower levels. Fig. 5 illustrates the flow sheet of the recommended process consisting of operations such as filtration, calcination, cooling etc. Facilities to recover the fines likely to be emanated during calcination and scrubbing the harmful emissions are also included in the system.

#### 4. CONCLUSIONS

Calcination at elevated temperature has been successfully employed to reduce the chloride content in iron oxide generated during acid regeneration of spent hydrochloric acid (produced by benelite process), to significant levels, thereby possibly enabling the iron oxide suitable for a variety of applications. The acidity level of the iron oxide has also been significantly reduced as a result of removal of significant chlorides through calcination. The diffraction pattern reveals the direct transition of magnetite to  $\alpha$ -hematite upon calcination. The changes in morphology upon calcining the iron oxide have also been studied in detail. According to the results, a process for calcinations and recovery of iron oxide has also been presented. This approach will allow interested parties to evaluate the advantages and further utilize the value-added iron oxide in their process. However the practical utility of the process requires full optimization of various process parameters and also economic assessment of the process.

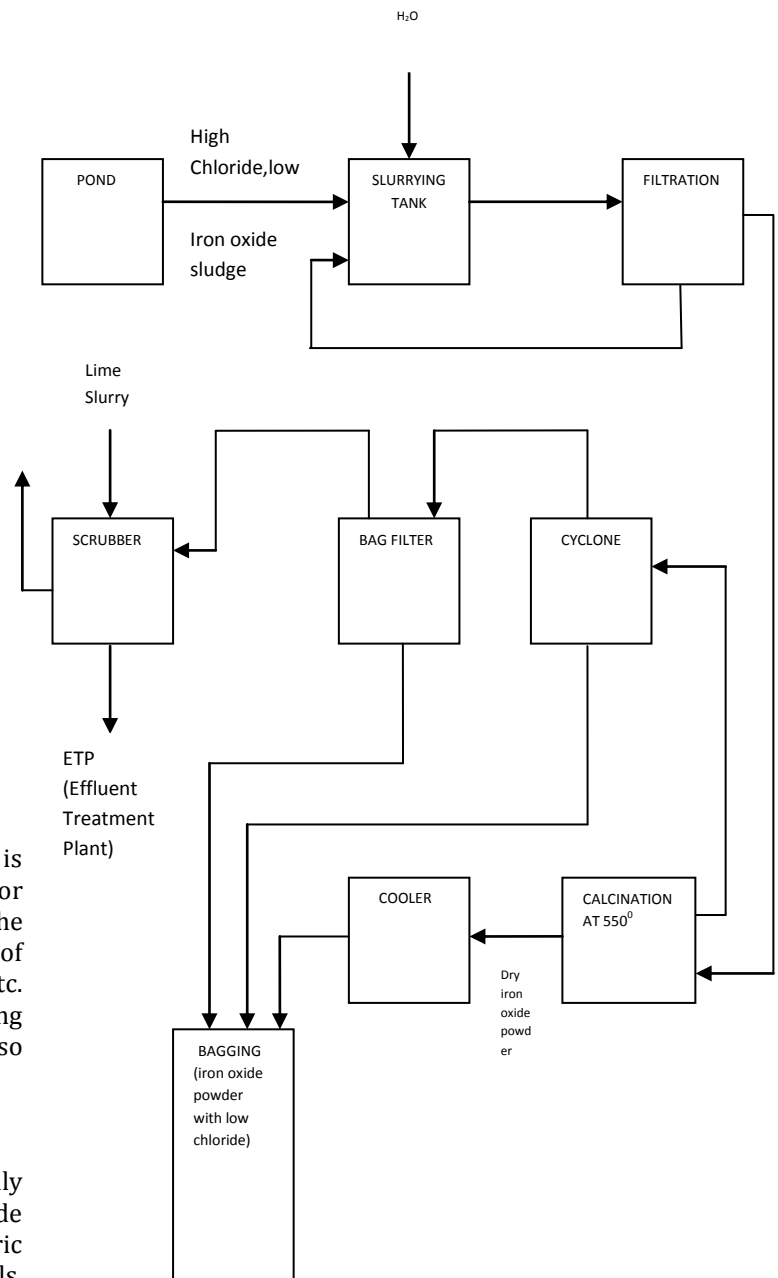


Fig -5: System proposed for implementing the calcination process

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## BIOGRAPHIES



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