Desired Development Aspects for Spray Roasted Iron Oxides
Predominantly for the Production of Ferrites

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Abstract:

Different grades of spray roasted iron oxides are produced in form of chemical by-products at steel mills. Originating from the thermal decomposition of up-graded iron chloride solutions, these synthetic iron oxides became a strategic raw material source for the production of soft and hard ferrites, and a series of chemical, ceramic and metallurgical products. Manganese contents in the order of 0.25 up to 1.0 per cent limit their usage for some applications, which presently being serviced by iron oxides based on other precursors. Another fast growing market concerns olivine structured LiFePO4 cathode battery materials, which contain about 50 wt.% Fe2O3. Spray roasters have been designed to yield iron oxides exhibiting specific surface area data in the range of 0.5 up to 25.0 m²/g. Preferred BET-data are: 0.5 up to 4.0 m²/g for hard ferrites, 3.0 up to 5.5 m²/g for soft ferrites and 8.0 up to 12.0 m²/g for pigments. Washed iron oxides exhibiting total chloride levels in the order of 600 ppm Cl- are available. Further washing results in Cl- levels of 300 ppm and an additional thermal treatment, by means of a short treatment within a vertical un-obstructed furnace, yields iron oxides with < 20 ppm Cl.

Key Words: Ferric oxide, Specific surface area, Residual chlorides

I. INTRODUCTION

It is about fifty years ago since the first regenerated spray roasted iron oxides have been produced at a small steel mill in Europe. Presently about 1.2000.000 metric tons per year of spray roasted iron oxides, originating from steel mills, service synthetic iron oxide markets on a global basis.

Spray roasted iron oxides have been used on an industrial scale for the production of soft and hard ferrites on an industrial scale at steel mills in Japan, USA and Europe since the year 1964. Regenerated synthetic iron oxides are produced from spent hydrochloric acid pickle liquors [1], [2]. Prior to the year 1964 most steel strip was pickled with sulfuric acid without any possibility of acid regeneration next to the pickling line.

### Table I Synthetic Fe2O3 produced by various processes

<table>
<thead>
<tr>
<th>Main Industrial Application</th>
<th>Sulfate Process</th>
<th>Chloride Process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Precipitation</td>
<td>Thermal Decomposition</td>
</tr>
<tr>
<td>Hard Ferrites</td>
<td>&lt; 0.5 %</td>
<td>60 %</td>
</tr>
<tr>
<td>Soft Ferrites</td>
<td>&lt; 0.5 %</td>
<td>20 %</td>
</tr>
<tr>
<td>Pigments</td>
<td>93 %</td>
<td>5 %</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>5 %</td>
<td>5 %</td>
</tr>
<tr>
<td>Recycled at steel mills</td>
<td>&lt; 0.5 %</td>
<td>10 %</td>
</tr>
</tbody>
</table>

Metric tons/Year 1.2000.000 1.200.000

Table I indicates, on an estimated basis, the world-wide industrial production of synthetic iron oxides by means of the sulfate - and chloride - routes and its industrial usage. Also about 1.200.000 metric tons per year of up-graded natural iron ore concentrates are generally being used for non-metallurgical purposes.
II. ACTUAL MATERIAL PROPERTIES OF SPRAY ROASTED IRON OXIDES

A. Specific Surface Area

Generally speaking, we have seen spray roasted iron oxides produced at steel mills exhibiting surface areas in the range of 1.0 up to 25.0 m²/g. Spray roasted iron oxides exhibiting a specific surface area of less than 1.0 m²/g may result in lower chloride contents, but are of no significant advantage for further ferrite raw material applications. Up-graded spray roasted iron oxides exhibiting specific surface areas in excess 10 m²/g (BET) are of interest for pigment applications. In order to produce spray roasted iron oxides exhibiting higher BET-data the design of the spray roaster, as well as required design features of the process, have to be modified.

B. Bulk Densities

Presently the largest share spray roasted iron oxides exhibit bulk densities of 450 +/- 50g/dm³. Upon dry milling, the preferred bulk density, for ferrite applications is around 800 g/dm³. Further increase in bulk density results in sometimes undesired powder sticking effects. Even it is possible to bring up the bulk density of spray roasted iron oxide by means of dry milling up to the range of 1200 g/dm³, it is not considered to be of advantage due to less uniform ferrite raw material mixtures. Higher bulk densities may be accomplished by means of wet processing and spray drying of spray roasted iron oxides up to bulk densities around 1850 g/dm³.

C. Accompanying Alloying Elements

The increasing manganese content in spray roasted iron oxides in the order of 0.2 up to 0.3 wt.% Mn is due to more recent metallurgical developments and of no significant disadvantage for the production of soft ferrites. Strontium hexaferrite producer may have a different point of view, due to the high vapor pressure of manganese oxides at elevated temperatures. For economic reasons it is presently too expensive to produce ‘manganese – free’ spray roasted iron oxides [3]. Also higher purity CPP-grade spray roasted iron oxides contain substantial and varying amounts of manganese oxides. To the extent of other alloying elements contained in spray roasted iron oxides, please consult the author’s contribution to ICF 10.

III. PRE-SINTERED FERRITE POWDERS

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Fig. 1 Exhibits the micro-structure of a pre-sintered MnZn-Ferrite powder, for high perm applications, prepared by means of a short heat treatment of a few seconds within an high vertical un-obstructed furnace. The fast reacted calcined ferrite powder exhibited a bulk density of 1500 g/dm³ and 5.1 m²/g (BET). An extremely short milling provided desirable steep primary particle size distribution. There is a good potential for shorter and respectively lower final ferrite compact sintering time and temperature. 70/15/15 (306)

Fig. 2 Exhibits the micro-structure of a pre-sintered, MnZn-Ferrite powder for power applications prepared by means of a short thermal treatment for a few seconds within an unobstructed vertical furnace. Related ferrite powder exhibited a bulk density of 1520 g/dm³ and 2.7 m²/g (BET). Subsequent short milling time provided desirable steep primary particle size distribution. There is a potential for shorter sintering times as well as lower ferrite compact firing temperatures. 71/21/08 (609)

Upon the time we finished the semi-industrial development, by end of the year 1999, the soft ferrite industry within the EU underwent dramatic changes and the core production declined drastically. Today energy saving issues in industrial countries as well as developing countries enjoy a higher degree of economic consideration. Ever since the turn of the millennium China became the largest producer of MnZn-ferrites on a world-wide basis. In the meantime in excess of 400.000 tons of a series of spray roasted iron oxides are produced locally. Local competition of MnZn-ferrite core and component producer in China resulted, along with large number of iron oxides producer, into a situation, that a large part of tested so-called energy saving lamps, all have been approved by EC authorities, did not save any energy at all [4], despite the fact, that high purity manganese and zinc oxides were locally available.

However, the consistency and quality and of spray roasted iron oxides for ferrite applications, depends on local circumstances within steel mills, which have to be considered more precisely. The difference between UPL-, PPP- and CPP-type spray roasted iron oxides have been published [4]. The main concern about spray roasted iron oxide quality, at present, are high and fluctuating residual chloride contents in the order of 600 up to 3000 ppm total Cl−, which should receive more concern in the near future. The calcining temperatures of soft ferrite raw materials are in the range of 820 °C. This temperature range is not sufficient to thermally decompose a number of metal chlorides [5], comprising contents of NaCl, KCl, CaCl₂, BaCl₂, SrCl₂ as well as NH₄Cl. For the steel industry spray roasted iron oxides are only considered a by-product, which helps to keep the plant clean.

The industrial water quality, within steel mills, depends on the season and dry summers yield higher impurity levels. For the production of PPP- and CPP-type spray roasted iron oxides de-mineralized water is being used, but the chloride level prior to subsequent washing operations is still in the order around 1500 ppm Cl⁻. Subsequent iron oxide washing operations, yield, depending on respective BET-data, Cl⁻ contents in the order of 500 ppm. Fluctuations of Cl⁻ contents within spray roasted iron oxides makes it difficult for ferrite producer to precisely control their ceramic process and ferrite consumer will have to pay the bill for the inferior performance of ferrite transformer cores, due to accumulated power losses.
For this reason it is desirable, that the iron oxide producer consider to further reduce the content of total Cl⁻ contained in spray roasted iron oxide substantially. Reducing the Cl⁻-level of spray roasted iron oxides to less than 300 ppm, for some application to less than 30 ppm will have definite advantages for envisaged micro-structure control for sintered MnZn-ferrite cores. Furthermore, everyone will experience less corrosion effects on ferrite powder processing equipment. Results of Cl⁻ removal by means of a short thermal treatment of a few seconds is indicated in Fig. 3 and Fig. 4.

Upon selecting the best spray roasted iron oxide sources at steel mills, we recommend to install a large, industrial scale, spray roasted iron oxide washing facility, outside steel mills, with a capacity in the order of 30,000 up to 50,000 annual tons yielding ‘Cl⁻-free’ iron oxides. At the same time it is an option to directly proceed with the production of high performance ready to press manganese zinc ferrite powders using, an energy saving vertical furnace in order to control micro-structure formation more precisely. Since about 85 % of soft ferrites are produced in China, urgently required developments along this line could be of global mutual benefit.

![Fig. 3. Reduction of Cl⁻ by means of a vertical indirectly heated unobstructed vertical furnace within two seconds from iron oxide granules exhibiting diameters in the range of 20 – 250 µm, depending on provided temperature.](image1)

![Fig. 4. Sprayed dried iron oxide granules with diameters of 20 – 250 µm. Reduction of specific surface area (BET) caused by a short heat treatment for about two seconds, employing an unobstructed vertical furnace.](image2)

**Fig. 5** SEM micro-structure image of a commercial low loss MnZn-ferrite core for power applications, exhibiting a loss at 100°C of 300 kW/m³ at 100 kHz and 200mT. It is considered, that this ferrite core has been prepared using washed iron oxides containing < 500 ppm Cl⁻.
For this reason it is desirable, that the iron oxide producer consider to further reduce the content of total Cl- contained in spray roasted iron oxide substantially. Reducing the Cl--level of spray roasted iron oxides to less than 300 ppm, for some application to less than 30 ppm will have definite advantages for envisaged micro-structure control for sintered MnZn-ferrite cores. Furthermore, everyone will experience less corrosion effects on ferrite powder processing equipment. Results of Cl- removal by means of a short thermal treatment of a few seconds in indicated in Fig. 3 and Fig. 4.

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Fig. 5  SEM micro-structure image of a commercial high loss MnZn-ferrite core for power applications, exhibiting a loss at 100°C of 600 kW/m³ at 100 kHz and 200 mT. It is considered, that this ferrite core has been prepared using washed iron oxides containing < 500 ppm Cl-.

C. Hard Ferrite Powders

The calcining temperatures for SrO.6Fe₂O₃ are much higher in comparison to soft ferrites, but the possibility to thermally de-compose SrCl₂, even at high temperatures, may not be considered to be of advantage for precise micro-structure control. Extensive subsequent milling operations will yield undesirable flat primary particle size distributions upon wet milling.

Tests carried out employing a short thermal treatment for about 3 seconds within an unobstructed industrial size vertical furnace [6] indicated, that it was not possible, even at temperatures of 1200 °C, to substantially reduce the chloride content. After the short thermal treatment resulting granules still contained about 60% of the original content corresponding to 900 ppm Cl-. In order to improve the micro-structure of oriented SrO.6Fe₂O₃ cores, it is also recommended to start from washed iron oxides, containing less than 300 ppm, preferably less than 30 ppm Cl-. There should be at least one iron oxide producing installation in an industrialized country, which is in a position to produce up-graded spray roasted iron oxides, containing only traces of Cl-. Investments along this line are of economic importance for the production of ferrites exhibiting an olivine type structure (LiFePO₄).

Further removal of residual chlorides is considered to be of importance for sintered ferrite products in general in order to control the final micro-structure. This fact becomes obvious by considering the thermal dynamic properties of metal chlorides, oxy–chlorides as well as organic auxiliary additives, which often only thermally decompose at higher temperatures and at the same time effect the micro-structure formation.

A larger scale annual production provides economic means to justify additional investments for further upgrading PPP- and CPP- type iron oxides. The world market prices for iron ores are presently in the order of > € 125,-/ton. This price level justifies additional investments for means to recycle spray roasted iron oxides within integrated steel mills, in order to avoid additional cost for analytical quality control, big bag handling, warehouse storage and international selling efforts.

Cold rolling mills have only limited analytical facilities and little opportunities to sell their regenerated iron oxide at a fair price. Several producers of UPL- type iron oxides sell their by-products without accepting any guarantees for quality control to the industries at any price just to avoid the deposition costs and in order to fulfill environmental restrictions. UPL- type spray roasted iron oxides are traded on the world market and many ferrite producer take advantage of any market situation. For several industrial ferrite products, even blending with natural iron or fines or mill scale, for less demanding ferrite powders, is still standard practice. However, there are a series of highly demanding ferrite products,
which require strict quality control for any ferrite raw materials and even more consistent up-graded spray roasted iron oxides are required.

IV. DISCUSSIONS

For the production of high performance soft and hard ferrite cores it is recommended to substantially reduce the chloride content of spray roasted iron oxides to by means of a washing operation, yielding in a first reduction step about 300 ppm of Cl-. After spray drying, a short heat treatment of iron oxide granules at higher temperatures may further reduce the chloride content to less than 20 ppm. I am convinced, from an economic point of view, that the reduction of Cl- has not yet received required attention in order to substantially reduce the loss factors of MnZn-ferrites cores for illumination as well as some other ferrite applications. Nearly Cl--free PPP-type spray roasted iron oxides, are also of advantage in order to further improve the performance of oriented strontium hexa-ferrite powders. Spray roasted iron oxides, exhibiting extremely low chloride contents, are considered to be essential for the production of precisely controlled uniform ferrite micro-structures.

ACKNOWLEDGEMENTS

The author would like to express many thanks to Mr. Anton Deruwe of ArcelorMittal, Belgium and Mr. Klaas Evers of ThyssenKrupp Steel Europe, Germany for providing analytical results related to spray roasted iron oxides.

REFERENCES