Providing High Purity Ferric Oxide to the Soft Ferrite Industry from a Steel Producer’s Point of View - Opportunities and Challenges

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Abstract

Especially in the production of MnZn- and NiCuZn-ferrites the purity of applied ferric oxide is of vital importance to achieve high quality products. Usually synthetic iron oxides produced by the spray roasting process of spent pickle liquor in flat carbon steel production are used. Spray roasting plants therefore have to be equipped with a pickle liquor purification process to remove elements like Ti, Al, Cr, P simultaneously by means of precipitation. Colloidal silica is bonded in parallel to a certain degree by means of adsorption on precipitated metal hydroxides. In recent years plenty of new steel grades have been developed requiring more and/or new alloying elements leading to an additional contamination of the pickle liquor and thus pushing the purification system to the limit. In order to overcome possible troubles additional treatment of spent pickle liquor prior to spray roasting has to be considered. In the case of Ni and Cu a removal of the pickle liquor by membrane electrolysis was investigated by operating a small pilot plant. Cu was removed completely and Ni removal was up to 20%. In case of Ni for quantitative removal also organic complex forming agents like Dimethylglyoxime can be applied.

Key Words: High Purity Ferric Oxide, Trace Elements

I. INTRODUCTION

A strong focus is kept on the level of impurities in ferric oxide used for high performance soft ferrites. In recent years facing more stringent regulations in terms of fuel economy and for safety reasons the automotive industry has been the driver for the development of various new high strength steel grades. Compared to traditional carbon steel grades additional or higher levels of alloying elements are required. In fact during pickling additional contamination of silica, Mn, Al, Ni, Cr, Nb and B may be introduced, pushing the purification system to the limit. Furthermore recycled steel scrap in the steel making process contributes to undesirable elements like Cu and Sn. As high strength steels are also used more and more in other applications, purification of pickling liquor has to cope with this development. Therefore additional treatment options have to be investigated.

II. MEMBRANE ELECTROLYSIS FOR NICKEL AND COPPER REMOVAL

In the galvanic industry for the recovery of noble metals as well as for Cu and Ni electrolysis is already applied at industrial scale [1, 2], also the regeneration of steel pickling liquors was investigated in recent years [3]. According to the electrochemical series listing the standard reduction potentials Ni^{2+} and Cu^{2+} should be reduced to their metals primarily to Fe^{2+}. Although in carbon steel pickling liquor the concentrations of Ni and Cu are rather low compared to Fe electrolysis was applied by means of small pilot plant. As a catholyte purified pickling liquor from the regeneration plant was taken (concentration ranges: Fe 163-165 g/l, Ni = 20 - 23 mg/l and Cu 4,2 - 5,6 mg/l).

Assumed reduction and oxidation reactions are indicated in fig 1. As cathodes aluminum plates with a usable surface of 4,83dm² were chosen. In order to avoid toxic Cl₂-formation at the anode according to 2Cl⁻ → Cl₂ + 2e⁻ the anodic region was separated by a cation exchange membrane which can only be permeated by positively charged ions. So oxygen evolution took place at the expanded metal anode made of titanium doped with Pt, Ir and Os. The anolyte was prepared as a solution with 50 g/l ammonium sulfate. By means of two rotary pumps (volume flow app. 100 l/h) the anolyte as well as the catholyte (each 12,9l kept in a storage tank) were kept in motion to provide a steady flow through the electrolysis chambers.

Preliminary tests indicated a minimum voltage to be applied ensuring a current flow and metal deposition in the range of 2,6V. As soon as voltage exceeded a level of 2,9 V the deposits grew in a dendritic way and thus in a short while endangered the installed cation exchange membrane. To ensure an evenly coverage of the cathode the voltage has to be kept in a range of 2,7 to 2,8 V. During an operation period of 12h per trial samples of the pickling liquor were taken and analyzed with regard to Fe (titration), Ni and Cu (ICP-OES Perkin Elmer 4300DV).
Evolution took place at the expanded metal anode made of titanium doped with Pt, Ir and Os. The anolyte was prepared as was separated by a cation exchange membrane which can only be permeated by positively charged ions. So oxygen analyzed with regard to Fe (titration), Ni and Cu (ICP-OES Perkin Elmer 4300DV). Additional or higher levels of alloying elements are required. In fact, during pickling, additional contamination of silica, Mn, Al, Ni, Cr, Nb and B may be introduced, pushing the purification system to the limit. Furthermore, recycled steel scrap in production are used. Spray roasting plants therefore have to be equipped with a pickle liquor purification process to remove elements like Ti, Al, Cr, P simultaneously by means of precipitation. Colloidal silica is bonded in parallel to a certain degree by means of adsorption on precipitated metal hydroxides. In recent years, plenty of new steel grades have been developed requiring more and/or new quality products. Usually, synthetic iron oxides produced by the spray roasting process of spent pickle liquor in flat carbon steel production are used. Spray roasting plants therefore have to be equipped with a pickle liquor purification process to remove elements like Cu and Sn. As high strength steels are also used more.

**I. INTRODUCTION**

Electrochemical series listing the standard reduction potentials Ni²⁺ and Cu²⁺ should be reduced to their metals primarily. The removal of Cu from spent pickle liquor is a rather complicated task, however. In the case of Ni and Cu, the maximum deposition rate was achieved at pH=1.67. The deposition rate declines with increasing and decreasing pH-levels. For Ni-reduction, the most favorable operation window seems to be linked to the pH-level. The bar chart indicates also that selectivity of Ni and Cu reduction is comparatively low as a vast amount of Fe is reduced.

The calculated average deposition rates over 12h for Cu, Ni, and Fe, the current density, and their dependencies from pH-level are shown in fig. 3. In the case of Ni and Cu, the maximum deposition rate was achieved at pH=1.67. The deposition rate declines with increasing and decreasing pH-levels. For Ni-reduction, the most favorable operation window seems to be linked to the pH-level. The bar chart indicates also that selectivity of Ni and Cu reduction is comparatively low as a vast amount of Fe is reduced.

**Fig. 1** Scheme of membrane electrolysis.

**Fig. 2** Membrane electrolysis of purified pickling liquor.

**Fig. 3** Deposition rates of Ni, Cu, Fe and current density at different pH-levels.

So for removal of Ni and Cu according to the trial represented in fig. 2, an energy demand of 15.9 kWh/m³ pickling liquor and 73 kWh/t of ferric oxide can be calculated, which is rather high as most of the energy is dedicated to Fe reduction.

**III. PRECIPITATION OF NICKEL**

In aqueous solutions Ni²⁺ precipitates as hydroxide at pH=8-10 [4]. Unfortunately at this level also Fe²⁺ and Fe³⁺ are already completely precipitated, thereby removal as hydroxide is impossible to perform in the pickling liquor purification unit of a regeneration plant. In order to overcome these troubles, the formation of solid complexes which are stable at pH = 3-4 may be an alternative. However, only compounds free of harmful tramp elements and without noteworthy cross-sensitivity to Fe²⁺ and Fe³⁺ are acceptable. Dimethylglyoxime (DMG) also referred to as diacetyl dioxime is a complex forming agent according to fig. 4. It is mainly used for gravimetric determination of Ni in aqueous solutions and applied at neutral to weak alkaline conditions [5]. The behavior of DMG in iron saturated pickling liquor derived from the regeneration plant was tested in a series of lab trials. Stirred pickling liquor samples of 200 ml were treated similarly to the purification system by adding ammonia solution (25 wt-%) to raise pH-value to approximately 4.

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At this stage Fe$^{3+}$, Al$^{3+}$, Ti$^{4+}$, Cr$^{3+}$ and PO$_4$$^{3-}$ precipitate. Additionally DMG was added, followed by a stirring period of 10 min. An anionic flocculation aid (25ppm) was added and for sludge removal the samples were filtered by means of a filter paper of Macherey-Nagel (MN 615) with pore size in the range of 4 – 12 µm. The obtained filtrates were analyzed with regard to Ni, Al, Si, Ti and P by ICP-OES.

![Fig. 5](image-url)  Reaction of DMG with Ni$^{2+}$ acc. to [5].

![Fig. 6](image-url)  Ni-concentration in dependency of added DMG.

The results of the trials are depicted in fig. 6 showing the lowering of Ni-concentration with progressive dosing of DMG reaching the limit of quantification of 0.5 mg/l Ni at a dosing rate of 250g/m³. The second vertical axis represents the calculated corresponding NiO concentration in ferric oxide. Fig 6 also indicates that overdosing is required to a certain extent. For Si, Al, Cr, Ti and P no differences by the introduction of DMG were obtained. The formed solids by adding DMG are very fine and therefore show a rather slow settlement. The slow rate of sedimentation is also expressed by the second data series in fig. 6. Therefore the treated pickling liquor samples were kept unmoved over 2h, afterward samples from the supernatant were taken and analyzed. The investigations show that Ni concentration can be reduced to a remarkable extent by the application of DMG. For a quantitative removal a filtering process shall be applied.

### III. CONCLUSION AND OUTLOOK

In terms of future development of steel grades the trend of increased use of alloying elements will continue. This challenge will only be mastered by R&D efforts in collaboration between supplier and customers. The current impurity level of several voestalpine’s ferric oxide products is shown in table 1. Up to now the challenge of increasing silica freights in pickling liquor has been successfully tackled. Silica is removed quantitatively in the case of grade HPG<20.

**Table I** Impurity level of several voestalpine’s high purity ferric oxide products – typical values [wt-%].

<table>
<thead>
<tr>
<th>Brand</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>MnO</th>
<th>NiO</th>
<th>CuO</th>
<th>Cr$_2$O$_3$</th>
<th>TiO$_2$</th>
<th>P$_2$O$_5$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>Cl</th>
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<tr>
<td>MHPG≤150 TW</td>
<td>0,011</td>
<td>0,002</td>
<td>0,65</td>
<td>0,013</td>
<td>0,003</td>
<td>0,001</td>
<td>0,001</td>
<td>0,002</td>
<td>0,006</td>
<td>0,006</td>
<td>0,09</td>
</tr>
<tr>
<td>HPG &lt;80 TW</td>
<td>0,007</td>
<td>0,002</td>
<td>0,50</td>
<td>0,013</td>
<td>0,003</td>
<td>0,001</td>
<td>&lt;0,001</td>
<td>0,002</td>
<td>0,006</td>
<td>0,006</td>
<td>0,09</td>
</tr>
<tr>
<td>HPG &lt; 60</td>
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<td>0,002</td>
<td>0,28</td>
<td>0,013</td>
<td>0,002</td>
<td>&lt;0,001</td>
<td>&lt;0,001</td>
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<td>0,004</td>
<td>0,004</td>
<td>0,09</td>
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<tr>
<td>HPG &lt; 20</td>
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<td>≤0,001</td>
<td>0,28</td>
<td>0,013</td>
<td>0,002</td>
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<td>&lt;0,001</td>
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### REFERENCES