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A NEW PROCESS FOR COPRECIPITATION OF FERRITES

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Résumé. — Une méthode utile de préparation des ferrites a été mise au point, par coprecipita-
tion de combinaisons préférentielles de carbonates et d'hydroxides métalliques. Ces combina-
ions fournissent des poudres dont on peut prédire la composition et qui présentent des bas niveaux
d'impuretés ainsi que des dimensions de grain et une réactivité optimales. Parmi les variables qui
sont contrôlées figurent le pH, la température, les taux d'addition et le degré d'agitation. Cette
méthode est utilisée pour la préparation de ferrites de Ni-Zn, de Mg-Mn et de Mn-Zn. Le contrôle
de la composition et du niveau d'impuretés est obtenu par un choix judicieux des matériaux de
base et du processus technique. La poudre ainsi produite peut être utilisée dans des systèmes con-
ventionnels de fabrication à sec des céramiques, les taux de retrait étant compatibles entre eux. Des
perméabilités élevées mesurées sur tores se combinent avec de faibles facteurs de pertes pour four-
nir des matériaux utilisés dans les applications aux télécommunications et en hautes fréquences.

Abstract. — A useful method of preparing ferrites has been developed by the coprecipitation of
preferred combinations of metal carbonates and hydroxides. These combinations give powders of
predictable compositions, low impurity levels and optimum particle sizes and reactivities. Some of
the variables which are controlled are pH, temperature, rates of addition and degree of agitation.
The method is used to prepare NiZn, MgMn, and MnZn ferrites. Control of composition and impu-
rity level is achieved by proper choice of raw materials and processing techniques. The powder
produced can be processed in conventional dry ceramic processing equipment because of matched
shrinkage ratios. High toroidal permeabilities and low loss factors are combined in components for
telecommunications and high frequency uses.

1. Introduction. — Coprecipitation is an attractive
method of producing ferrites because of increased
homogeneity, purity, and reactivity over standard
ceramic processing. The chemical species most fre-
cently used are the hydroxides, oxalates, and carbo-
nates. The hydroxides are gelatinous, leading to
filtration difficulty and, in addition, cause loss of some
ions by complexing, particularly when ammonia is the
precipitant. Oxalates are costly to produce and the
oxalic acid cannot be recycled. Carbonates do not
form from aqueous ferric solutions and when formed
from ferrous salts, give poor ceramic reactivity when
decomposed. Takada [1] modified the hydroxide
method by bubbling air through the slurry to convert
to ferrites. Cores produced by Akashi [2] from powder
using this method had excellent magnetic properties.

2. Experimental. — 2.1 Preparation of solu-
tions. Mn-Zn ferrites. — An important aspect of
this process was the very exact control of final com-
position through the use of the pure metals as starting
materials. The desired molar ratio of metals was
weighed out and dissolved in sulfuric acid. A small
excess of the acid over the stoichiometric amount was
necessary to prevent hydrolysis. Heat and agitation
accelerated the solution. The total metal content
was designed to be about 1.5 M. The individual metal
ion concentrations were analyzed and found to be
close to those predicted from the original metal
contents. The weight of the metals used were
66-72 % Fe, 10-23 % Mn, and 5-18 % Zn. A second
solution containing 1 M ammonium hydroxide and
1-2 M ammonium bicarbonate was made up. The water
used in the metals and base solutions had a resistivity
of 18 million ohms.

2.2 Precipitation of carbonate hydroxide mix-
ture. Mn-Zn ferrites. — The carbonate-hydroxide
solution having a pH of about 11 was placed in large
container and the metallic salt solution introduced
with good agitation. The pH was monitored and when
the desired pH was reached, the flow of sulfate solu-
tion was stopped. The precipitate was separated from
the mother liquor by either centrifugation or vacuum
filtration. The precipitate was washed with deionized
water of above purity until the acidified BaCl₂ test
was negative showing the absence of sulfates. The
precipitate was then analyzed for CO₃⁺/OH⁻ ratio by removing a sample, adding a measured excess
amount of standardized dilute sulfuric acid, measuring
the evolved CO₂ and then back-titrating the excess
acid with standardized sodium hydroxide solution.
The individual metal contents of the mother liquor
after filtration were analyzed by titration with dichro-
mate and by atomic absorption techniques.

2.3 Drying and calcining precipitate. — The
precipitate was then dried at between 150-200 °C.
Partial decomposition of the carbonate occurred as
well as oxidation of the ferrous compounds to ferric. The dried precipitate was then broken up and calcined either in a batch furnace or in a rotary calciner. Calcining temperatures ranged between 600-800 °C. The mole percents of the metal ions were determined by X-ray fluorescence technique.

2.4 Precipitation of other ferrites. — For the Ni-Zn ferrites, the corresponding sodium compounds and for Mg-Mn ferrites, potassium compounds were used in place of ammonium salts to preclude complexing of the Ni. Other features of the method were as described above, except that the Mg-Mn ferrites, after addition of the sulfate solution to the carbonate solution, the precipitation reaction was accelerated by boiling the solution for 5 minutes.

2.4 Preparation of cores from Mn-Zn powder. — The calcined powder was ball-milled until the average particle size was 1.0 µm. A PVA binder was added and the slurry spray-dried. Toroids with an O. D. of 1" were pressed from the resultant powder, burnt off, and fired at a temperature of 1 180-1 200 °C. The atmosphere was changed during the cool to maintain the equilibrium O₂ value corresponding to the temperature [3].

2.5 Surface area measurements. — The surface area measurements were made on the Monsorb Surface Analyzer [4] which makes use of the nitrogen absorption technique, the nitrogen being carried by a stream of argon. The equipment gave results comparable to standard BET methods.

3. Results. — 3.1 Stoichiometry and completeness of precipitation in Mn-Zn ferrites. — Figure 1 shows the variation of percent of metals lost in the filtrate as a function of final pH. At a pH of 6, a large fraction of the metals appear in the filtrate. It should be pointed out that no attempt was made to separate the fine and colloidal particles from the dissolved metals in the filtrates. However, in a practical sense, it is the total metals lost in filtration that matters. Table I, showing the molar composition of the filtrate, indicates which elements are lost. At the pH of 6, the Fe and Mn are the elements not caught on filter. The filtrate appeared to contain much fine and colloidal matter, which accounts for the iron lost. At a pH of 9, about 3% of the metals is lost and almost all the loss is attributed to complexing of the Zn²⁺. At a pH of 8, even though the total metal lost is small, it is predominantly zinc. Figure 2 shows the mole percents of the metals in the dried carbonate powder as a function of final pH. The decreased iron content in the powder which had been precipitated at a pH of 6 agrees well with the loss of iron in the corresponding filtrate. Also, the high Zn content in the filtrate at a pH of 9 accounts for the low Zn content in the powder produced in that precipitation.

Table I

<table>
<thead>
<tr>
<th>pH</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>61.2</td>
<td>38.19</td>
<td>0.61</td>
</tr>
<tr>
<td>7.5</td>
<td>0.0</td>
<td>36.55</td>
<td>63.45</td>
</tr>
<tr>
<td>8.0</td>
<td>0.0</td>
<td>8.19</td>
<td>91.81</td>
</tr>
<tr>
<td>9.0</td>
<td>0.06</td>
<td>0.25</td>
<td>99.69</td>
</tr>
</tbody>
</table>

Table II shows the dependence of the loss of metals in the filtrate on the concentration of carbonate in the precipitant. At low concentrations of CO₃⁻ there is appreciable loss of metals. When an excess of carbonate is added, the loss is small. Table III gives the mole percents of the elements in the dried carbonate powder as a function of CO₃⁻ molarity in the precipitant. Also variations in temperature, flow rate, agitation and order of addition give small variations in stoichiometry.
**Table II**

*Weight percent of metals lost in filtrate as a function of carbonate concentration in precipitant*

<table>
<thead>
<tr>
<th>CO$_3^-$ Molarity</th>
<th>Weight percent of metals lost in filtrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50.29</td>
</tr>
<tr>
<td>0.44</td>
<td>39.56</td>
</tr>
<tr>
<td>1.05</td>
<td>0.03</td>
</tr>
<tr>
<td>1.75</td>
<td>0.14</td>
</tr>
<tr>
<td>2.0</td>
<td>0.13</td>
</tr>
</tbody>
</table>

**Table III**

*Mole percents of elements in dried precipitate as a function of CO$_3^-$ Molarity in precipitant*

<table>
<thead>
<tr>
<th>CO$_3^-$ Molarity</th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>53.1</td>
<td>31.5</td>
<td>15.4</td>
</tr>
<tr>
<td>0</td>
<td>61.24</td>
<td>5.89</td>
<td>32.86</td>
</tr>
<tr>
<td>0.44</td>
<td>47.57</td>
<td>28.08</td>
<td>24.35</td>
</tr>
<tr>
<td>1.05</td>
<td>53.42</td>
<td>31.53</td>
<td>15.05</td>
</tr>
<tr>
<td>1.75</td>
<td>53.75</td>
<td>30.74</td>
<td>15.51</td>
</tr>
<tr>
<td>2.0</td>
<td>53.54</td>
<td>31.24</td>
<td>15.22</td>
</tr>
</tbody>
</table>

3.2 Carbonate-Hydroxide Ratio in the Wet Precipitate. — Figure 3 gives the dependence of the mole percent of metal as carbonates in the precipitate as a function of pH. The percent carbonate increases until a pH of 8 is reached and at a pH of 9, the metal hydroxide percent actually becomes higher than the CO$_3^-$.. Figures 4 gives the same carbonate molar percent as a function of molarity of carbonate in the precipitant. As expected, it increases with CO$_3^-$ content in the precipitant. The carbonate-hydroxide ratio was also somewhat sensitive to the same processing variables listed above under Stoichiometry.

3.3 Surface Area of the Dried Precipitate. — Figure 5 shows the surface area in m$^2$/g as a function of the final pH. The surface area decreased sharply between pH of 6 and 7 and then increases slowly with increasing pH. The surface areas are extremely high, in general, leading to high reactivity in calcining. Figure 6 shows the surface area as a function of CO$_3^-$ molarity in the precipitant. The surface area increases...
markedly as the $CO_3^= \text{ content goes up. This also corresponds to the carbonate content in the slurry (see Fig. 4).}$

3.4 STOICHIOMETRY OF Ni-Zn FERRITES AND Mg-Mn FERRITES. — In the case of the nickel-zinc ferrites, since metal salts were used for the preparation of the sulfate solution, the stoichiometry of the dried precipitate was less predictable than in the Mn-Zn ferrites. Table IV shows the comparison between the mole percentage of the prepared solutions and that of the dried precipitate. Considering the uncertainty in the hydration of the salts, the agreement is fairly good.

The same is true for the Mg-Mn. Table IV shows a similar comparison and again the results are about the same as for Ni-Zn.

**TABLE IV**

*Comparison of calculated and observed mole percents in coprecipitated Ni-Zn and Mg-Mn ferrites*

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Mn</th>
<th>Zn</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Observed</td>
<td>49.5</td>
<td>25.2</td>
<td>25.3</td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>50</td>
<td>20</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Observed</td>
<td>51</td>
<td>20.5</td>
<td>28.5</td>
<td></td>
</tr>
</tbody>
</table>

In both the Ni-Zn and MgMn ferrite preparations, the disadvantage over the Mn-Zn procedure is in the presence of the alkali metal ions and the need for their removal.

4. Discussion. — 4.1 STOICHIOMETRY. — For solutions with a pH below 7, the $CO_3^= \text{ content is reduced by evolution of } CO_2$. Some of the iron is oxidized to $Fe_2O_3$ which is lost through its colloidal nature of fine particles. Between 7 and 8.5, with a sufficient excess (about 20%) of carbonate in the precipitant, almost complete precipitation is achieved. At pH of 9 and above, Zn is lost even with large excess of carbonate. Zn is known to form complexes both with $OH_-$ to form complex zincate ions, as well as with $NH_3$ to form complex ammines.

Because the solubility products of the carbonates of the three metals do not vary very greatly, the order of precipitation should not be very important. The same is true for the hydroxides of $Fe^{2+}$, $Mn^{2+}$, and $Zn^{2+}$. Using the $Fe^{2+}$ instead of $Fe^{3+}$ avoids the preferential precipitation of the very insoluble $Fe(OH)_3$ over the other two hydroxides.

4.2 CARBONATE-HYDROXIDE RATIO. — With high $CO_3^=$ concentrations, the carbonates are made to precipitate rather than the hydroxides. As the pH is raised or the $CO_3^=$ content lowered, the hydroxide precipitation can become appreciable. Manipulation of the various parameters can vary the ratio of carbonates to hydroxides over a wide range. This ratio will affect the reactivity of the powders in the calcining process and ultimately in the firing process.

4.3 SURFACE AREA. — After drying, precipitates which are very high in carbonates give high surface areas. Those which are predominantly hydroxides appear to give low surface areas. This is due to the strong agglomeration of the particles as hydroxides. Without a certain amount of hydroxides in the precipitate, the calcined material appears quite dead, very fine, and very difficult to densify in the firing process, especially without the use of high temperatures. The compromise appears to be one between using enough carbonate groups for ease of filtration and compositional integrity but having enough hydroxide groups to *cement* the particles together, possibly by some hydrogen-bonding mechanism.

4.4 MAGNETIC RESULTS OF CORES. — Powders produced by this method were subjected to the same processing as that produced by conventional techniques and pressed in the same dies. A comparison of the properties of cores using the two types of powder is shown in table V. The powder derived from coprecipitation techniques was used to prepare gapped pot cores. One such core, an 18 $\times$ 11 mm size, gapped to a 250 A is compared with a similar pot core from conventionally-produced material in figure 7.

**TABLE V**

*Comparison of magnetic properties of cores made from conventionally produced and coprecipitated powders.*

<table>
<thead>
<tr>
<th></th>
<th>Conventional Powder</th>
<th>Coprecipitated Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability</td>
<td>2000</td>
<td>2300</td>
</tr>
<tr>
<td>Loss factor $\mu Q$</td>
<td>$2 \times 10^{-6}$</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Disaccommodation</td>
<td>$5 \times 10^{-6}$</td>
<td>$5.0 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

![Comparison of Q vs frequency for pot cores using conventional and coprecipitated powders.](image)
4.5 Economics of the Process. — As noted previously, the process requires very pure metals, pure water, and costly ammonia. In addition, large reaction vessels are required and although initial mixing is omitted, calcining and all the other conventional processing steps are required with the new material. On the other hand, low temperature calcining and firing do incur an economy in energy. In addition, the ammonia and ammonium bicarbonate can be recycled in a manner shown in figure 8. The mother liquor from precipitation is reacted with slaked lime and the ammonia liberated. The ammoniacal solution is distilled to yield a concentrated ammonia water which can then be partially carbonated to produce a desired ammonium carbonate-ammonium hydroxide precipitant. In addition to saving the high cost of ammonia, the problem of disposal of the waste-by-products is eliminated.

References


[4] Monsorb Model MS-4, Quantachrome Corp, 337 Glen Cove Road, Greenvale, NY 11548 USA.