

Mathematical modeling of the magnetic-paper preparation process

JORGE A. CARRAZANA GARCIA AND M. A. LÓPEZ QUINTELA

ABSTRACT

The influence of six reaction variables on nine properties of magnetic paper was investigated. Magnetic properties were imparted through *in situ* synthesis of cobalt ferrites and then charging these particles into the cellulose fibers during a lumen-loading step. As a first hypothesis, a multilinear model was selected in which the coefficients of the codified variables were calculated using linear regression by combining two-factorial partial (2^{6-3}) experimental plans. Rather than predicting exact numerical values, the model gives the sign and relative magnitude of the variable coefficients, thus emphasizing the direction for improving magnetic and nonmagnetic properties. The results reveal some interesting trends. Above 40°C (the lower temperature limit for spinel formation via coprecipitation), the synthesis temperature does not play a significant role in any of the studied responses except crystallite size. However, higher pulp consistencies improve the ferrite properties. This indicates the importance of the nature of the particles formed in the presence of fibers during the *in situ* synthesis step. The validity of these and other observations was confirmed in subsequent experiments in which the reaction conditions were adjusted in the directions shown by the mathematical models.

Application:

Preliminary studies to identify optimum reaction conditions for production of magnetic papers.

PAPER HAS LONG BEEN THE TRADITIONAL medium for storing and distributing information. However, advances in electronic, magnetic, and optical media are forcing the paper industry to look for new opportunities to stay in this market. Production of papers with magnetic properties is an interesting possibility that may help the industry face this challenge. Potential applications for magnetic papers (1-3) include magnetic recording, electromagnetic shielding, security papers, magnetic filtering and fixing of products, and new concepts in handling and detection of papers (4, 5).

Magnetic paper can be produced by synthesizing ferrites in the presence of cellulose fibers in an aqueous phase (*in situ* synthesis step) and then charging these particles into the fibers' internal cavity (lumen-loading step) (6). This procedure takes advantage of two interesting properties of paper pulps: the cellulose chain's capacity for associating with cations (because of the presence of acidic groups in its structure), and the possibility of charging the fiber lumen with inorganic materials with minimal damage to the fiber's papermaking properties.

Ferrites are formed by careful oxidation of the $M(\text{OH})_2$ ($M = \text{Fe}$ and, eventually, other divalent transition metal cations) that precipitates when NaOH is added to a pulp suspension containing soluble salts of M . Two types of ferrite particles are formed: Larger particles (30-120 nm, depending on M and x in $M_x\text{Fe}_{3-x}\text{O}_4$) form in the bulk of the liquid phase,

while smaller particles (<10 nm) are directly associated with the cellulose matrix, where the cations are clamped to the polymeric chains by ionic exchange. With vigorous stirring of the suspension, the larger ferrites in the suspension can enter the fiber lumen through apertures (pits) in the fiber walls, where they are adsorbed. During washing, the particles that have not been incorporated into the fibers are easily removed, leaving a clean fiber surface available for interfiber bonding.

If the ferrous ions in the starting solution are partially replaced with Co^{2+} ions, it takes only one synthesis cycle to obtain coercive forces (H_c) that are high enough to be of interest for magnetic recording and many other applications proposed for magnetic papers. There are other substitutes for Fe (Ni, Mg, Mn, or Zn), but cobalt provides the highest magnetic properties. However, the presence of cobalt (II) and nickel (II) as substituents for ferrous ions promotes the formation of large glassy particles (typically plates >0.25 μm) as a side effect. In the filtering step (described later in this article), these large platey materials are retained on the same side of the sieve as the fibers. The particles interfere with bonding and consequently reduce sheet mechanical properties. Moreover, they consume chemicals and have poor magnetic properties, which diminishes the performance of the magnetic paper. (Note that the coercivity of the glassy particles and that of crystallized ferrite differ sharply, so their simultaneous pres-

ence can be detected as two peaks in the first derivative of the magnetization curve measured on the paper (7)). Clearly, these glassy particles must be eliminated to improve the mechanical and magnetic performance of the papers.

Response variable	Units	Description
$Y_1 = H_c$	oersted	coercive force of the magnetic paper (measured at room temperature)
$Y_2 = M_r$	emu*/g of paper	specific remanent magnetization of the magnetic paper
$Y_3 = M_s$	emu/g of paper	specific saturation magnetization of the magnetic paper
$Y_4 = \text{Ash}$	wt.%	ash content of the magnetic paper (corresponds to the total ferrite particles in the paper)
$Y_5 = M_{r,\text{ash}}$	emu/g of ash	remanent magnetization of ash (corresponds to remanent magnetization of ferrite particles in the paper)
$Y_6 = M_{s,\text{ash}}$	emu/g of ash	saturation magnetization of ash (corresponds to saturation magnetization of ferrite particles in the paper)
$Y_7 = \text{Peaks}_{\text{max}}$	...	number of maximums in the first derivative of the paper hysteresis curve (corresponds to formation of glassy particles joined to the crystallized ferrite)
$Y_8 = d_{311}$	nm	crystallite size of ferrite particles (calculated from the 311 X-ray diffractogram reflection)
$Y_9 = \text{Sq} (=M_r/M_s)$	...	squareness of the hysteresis cycle measured on the magnetic paper

* emu = electromagnetic units

I. Nine response variables

Run No.	INDEPENDENT VARIABLES					
	X_1	X_2	X_3	X_4	X_5	X_6
1	-1	-1	-1	+1	+1	+1
2	+1	-1	-1	-1	+1	-1
3	-1	+1	-1	-1	-1	+1
4	+1	+1	-1	+1	-1	-1
5	-1	-1	+1	+1	-1	-1
6	+1	-1	+1	-1	-1	+1
7	-1	+1	+1	-1	+1	-1
8	+1	+1	+1	+1	+1	+1

II. Experimental matrix for Part I of the study

There are many reaction parameters that can affect the final properties of magnetic papers. In such cases, a variable-by-variable investigation is not the most efficient technique for identifying ways of improving the performance of magnetic papers. A statistical experimental design is the better choice (8).

EXPERIMENTAL

Experimental plan

The objective functions in the statistical design all have the form

$$Y_j = \beta_0 + \sum_{i=1}^n \beta_{X_i} X_i$$

where Y_j represents the properties measured and X_i the independent variables. The nine response parameters ($j = 9$) measured on the paper and ferrite samples are listed in Table I.

Coded variables were used because the values of the coefficients β_{X_i} give the relative influence of each X_i , even when their natural values differ widely. (For example, the initial concentration of Fe^{2+} can have numerical values three orders of magnitude lower than the synthesis temperature.) With six variables ($n = 6$) at two levels each (+1 and -1), the minimum number of experiments required to obtain the regression equation is $2^6 = 64$ experiments. The complete equation would encompass the effects of all possible combinations between the variables (double, triple, ..., sextuple effects). However, most of this information has no physical sense. Moreover, in a first approximation to the problem, the relative influence of the independent variables is the only interest. The number of experiments can be drastically reduced using a partial experimental plan. The approach used (9) is as follows.

In a 2^{n-p} = 2^{6-3} plan, $2^3 - 1 = 7$ generators are needed where $p = 3$ are independent. In Part 1 of this study (eight runs), the levels of X_1 , X_2 , and X_3 were fixed according to a factorial design. For the remaining three variables, the following identities were used:

$$\begin{aligned} X_4 &= X_1 X_2 \\ X_5 &= X_2 X_3 \end{aligned}$$

$$X_6 = X_1 X_3$$

The generators were

$$\begin{aligned} I &= X_1 X_2 X_4 \\ I &= X_2 X_3 X_5 \\ I &= X_1 X_3 X_6 \\ I &= X_4 X_5 X_6 \end{aligned}$$

(Note that any one of these generators can be obtained from the other three.) Table II shows the experimental matrix for the first eight runs.

Neglecting the interactions of more than two variables at a time, the coefficients calculated in Part 1 include the influence of one single variable plus two double effects:

$$\begin{aligned} \beta_1 &= (\beta_{X_1} + \beta_{X_2 X_4} + \beta_{X_3 X_6}) \\ \beta_2 &= (\beta_{X_2} + \beta_{X_1 X_4} + \beta_{X_3 X_5}) \\ \beta_3 &= (\beta_{X_3} + \beta_{X_1 X_6} + \beta_{X_2 X_5}) \\ \beta_4 &= (\beta_{X_4} + \beta_{X_1 X_2} + \beta_{X_5 X_6}) \\ \beta_5 &= (\beta_{X_5} + \beta_{X_2 X_3} + \beta_{X_4 X_6}) \\ \beta_6 &= (\beta_{X_6} + \beta_{X_1 X_3} + \beta_{X_4 X_5}) \end{aligned}$$

$$\beta_0 = \text{estimate of the average for Part 1 (first eight runs)}$$

In the next eight runs (Part 2), X_1 , X_2 , and X_3 had the same values as in Part 1, but for the construction of the experimental matrix, the following identities were used for the remaining three variables:

$$\begin{aligned}X_4 &= -X_1X_2 \\X_5 &= -X_2X_3 \\X_6 &= -X_1X_3\end{aligned}$$

The generators for the Part 2 experiments were

$$\begin{aligned}I &= -X_1X_2X_4 \\I &= -X_2X_3X_5 \\I &= -X_1X_3X_6 \\I &= -X_4X_5X_6\end{aligned}$$

In Part 2, the calculated coefficients represent the following combined influences:

$$\begin{aligned}\beta_{2_1} &= (\beta_{x_1} - \beta_{x_2x_4} - \beta_{x_3x_6}) \\ \beta_{2_2} &= (\beta_{x_2} - \beta_{x_1x_4} - \beta_{x_3x_5}) \\ \beta_{2_3} &= (\beta_{x_3} - \beta_{x_1x_6} - \beta_{x_2x_5}) \\ \beta_{2_4} &= (\beta_{x_4} - \beta_{x_1x_2} - \beta_{x_5x_6}) \\ \beta_{2_5} &= (\beta_{x_5} - \beta_{x_2x_3} - \beta_{x_4x_6}) \\ \beta_{2_6} &= (\beta_{x_6} - \beta_{x_1x_3} - \beta_{x_4x_5})\end{aligned}$$

β_{2_0} = estimate of the average for Part 2 (second eight runs)

Working with the results of both Parts 1 and 2, it is possible to obtain the influence of each single variable:

$$\begin{aligned}\beta_{x_1} &= (\beta_{1_1} + \beta_{2_1}) / 2 \\ \beta_{x_2} &= (\beta_{1_2} + \beta_{2_2}) / 2 \\ \beta_{x_3} &= (\beta_{1_3} + \beta_{2_3}) / 2 \\ \beta_{x_4} &= (\beta_{1_4} + \beta_{2_4}) / 2 \\ \beta_{x_5} &= (\beta_{1_5} + \beta_{2_5}) / 2 \\ \beta_{x_6} &= (\beta_{1_6} + \beta_{2_6}) / 2\end{aligned}$$

which leads to the desired equation.

After some preliminary experiments (6), and using the experience of previous works (10, 11), the six variables shown in **Table III** were chosen. To conserve the stoichiometric relations, X_3 and X_5 were defined as molar ratios rather than absolute quantities.

For a particular run, the values of X_1 , X_2 , and X_6 represent directly the value of the corresponding natural variable. The weight of FeCl_2 is cal-

culated from X_4 and the volume of the suspension. The weight of CoCl_2 depends on X_3 and on the number of moles of Fe, which is related to X_4 . Finally, the weight of NaOH depends on the value of X_5 and both the values of X_3 and X_4 . As an example, the calculations corresponding to experiment No. 1 are as follows:

$X_1 = -1 \Rightarrow$ synthesis temperature = 40°C

$X_2 = -1 \Rightarrow$ NaOH added as solid

$X_6 = +1 \Rightarrow m(\text{pulp}) = 4 \text{ g}$

$X_4 = +1 \Rightarrow c(\text{Fe}^{2+}) = 0.15M$
 $\Rightarrow m(\text{FeCl}_2) = 5.964 \text{ g}$

$X_3 = -1 \Rightarrow \text{Co/Fe} = 1/20$ and $c(\text{Fe}^{2+}) = 0.15M$
 $\Rightarrow c(\text{Co}^{2+}) = 0.0075M$
 $\Rightarrow m(\text{CoCl}_2) = 0.357 \text{ g}$

$X_5 = +1 \Rightarrow M^{2+}/\text{OH}^- = 0.5$
 $\Rightarrow c(M^{2+}) = [c(\text{Fe}^{2+}) + c(\text{Co}^{2+})] = 0.1575M$
 $\Rightarrow c(\text{OH}^-) = 0.315M$
 $\Rightarrow m(\text{NaOH}) = 2.52 \text{ g}$

The experiments in Parts 1 and 2 were performed in random order, and the corresponding samples of magnetic paper and ferrite particles were analyzed to measure the values of the nine responses. With all this information, the multilinear fitting is attained using matrix operations to compute the values of the coefficients for the mathematical models.

Materials

Chemicals used were p.a. grade NaOH (Aldrich) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck) without further purification. The solutions and suspensions were prepared with bidistilled water. No special care was taken to isolate the system from atmospheric oxygen. In fact, oxidation from Fe^{2+} to Fe^{3+} (necessary for ferrite formation) is achieved by means of the dissolved O_2 , mainly during stirring. The fiber source was chemical semibleached pulp obtained from sugar cane bagasse. Sheets were dried and pressed in a laboratory press (Gumix 1403) with heated plates capable of applying pressure up to 100 kg/cm².

Independent variables	CODED VALUE		
	-1	0	+1
X_1 = temperature, °C	40	65	90
X_2 = addition of NaOH	solid	aq	aq
X_3 = Co/Fe ratio	1/20	1/5	1/3
X_4 = $[\text{Fe}^{2+}]$ init., mole/L	0.05	0.1	0.15
X_5 = M^{2+}/OH^- ratio	0.3	0.4	0.5
X_6 = weight of pulp, g	0.8	2.4	4

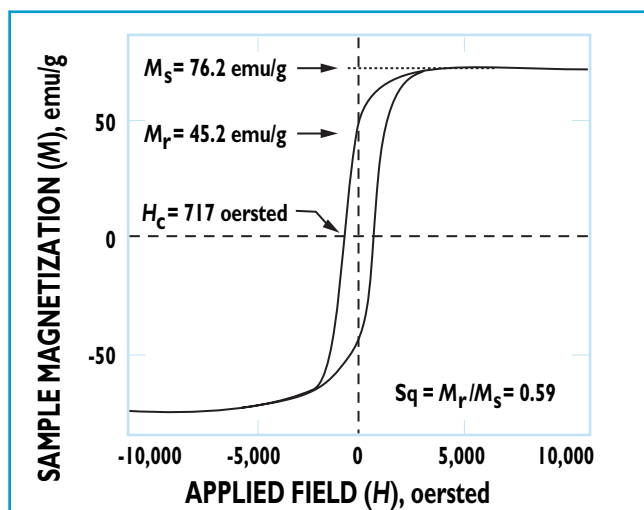
III. Coded and natural values of the experimental variables

Analytical techniques

Structural analysis. Structural analysis was performed in an automatic powder X-ray diffraction system (goniometer Philips PW 1820) with Cu K α radiation and automatically matched with a database (TADD+40). In the routine analysis, the spectra were taken at 0.01° steps and 1 s per step. For crystallite size calculations, the (311) reflection was measured from 34.5° to 36.5° (in 2 θ) at 11 s per step and fitted to a Gaussian profile. The medium crystallite diameter was calculated with the Scherrer equation using a KCl standard to estimate the instrumental contribution to peak width (APD 3.5B software) (12).

Paper ash. Paper ash was measured by drying the sheet at 105°C overnight and then burning in an oven for 4 hours at 925°C. After proper characterization (13), the ash content of the magnetic papers can be used as a secure measure of the ferrite included in the samples. The ash content of the pure paper pulp was determined separately for correction purposes, giving a value of 0.38% in weight, which was one or two orders of magnitude lower (depending on the charging level achieved) than the contribution of the particles incorporated into the paper during the magnetization process.

Magnetic measurements. The dc magnetization curves were registered at room temperature in a vibrating sample magnetometer (Digi-



1. Hysteresis cycle for a floppy disk (a typical standard in magnetic recording) illustrates relevant magnetic parameters

tal Measurement Systems, signal processor model 1660). The papers were cut into rectangular samples of 15 mm × 18 mm and measured parallel to the field. (Strong dependence between the magnetization values and the size and position of the sample was detected. The H_c value is not affected by these changes.) Saturation (M_s) and remanent (M_r) magnetization are related to the ash content and to the mass of paper sample. Figure 1 shows a graphic definition of the measured parameters.

Method

The procedure was carefully controlled in an effort to standardize the method such that the observed changes could be related only to the independent variables.

Dispersion. The mass of paper pulp corresponding to the experiment (variable X_6) is poured in 200 mL of distilled water and stirred for one hour at fixed speed. The reaction vessel is submerged in a thermostatic bath whose temperature is controlled at the value specified by X_1 .

Synthesis. When the pulp suspension reaches the desired temperature, stirring is reduced and the salts (MCl_2) are added. After 1 min (to allow ionic exchange), the NaOH is added either as a solid or in solution (according to X_2). One hour of reaction time is counted from the moment when the addition of NaOH begins.

Impregnation. The reaction vessel is removed from the thermostatic bath and submitted to vigorous stirring (2000 rpm) for one hour.

Filtering. The suspension is filtered with a 0.25-mm sieve. The ferrite particles separated from the pulp suspension in this step are washed, dried, and saved for future analysis.

Washing. Washing is performed in a discontinuous way. The magnetized pulp is redispersed in 400 mL of water and stirred for 10 min. The suspension is then filtered to separate the washed particles. When the mass of pulp was 4 g, this procedure was repeated five times. At the lower levels of X_6 (0.8 g and 2.4 g of pulp), only three washes were made.

Sheet forming. The suspension of magnetized washed fibers is filtered in a Büchner funnel. The pulp pad is then dried and pressed overnight at 105°C and 40 atm between stainless steel plates.

Expt. No.	RESPONSE VARIABLES								
	H_c , oersted (Y_1)	M_r , emu/g pulp (Y_2)	M_s , emu/g pulp (Y_3)	Ash, wt.% (Y_4)	$M_{r,ash}$, emu/g ash (Y_5)	$M_{s,ash}$, emu/g ash (Y_6)	Peaks (Y_7)	d_{311} , nm (Y_8)	Sq (M_r/M_s) (Y_9)
PART I									
1	303	0.54	1.87	13.1	4.12	14.27	1	28	0.29
2	41	0.0076	0.082	3.77	0.202	2.175	1	56	0.09
3	538	0.86	2.09	4.8	17.92	43.54	1	45	0.41
4	317	1.7	5.15	8.4	20.24	61.31	1	46	0.33
5	398	0.3	1.38	8.3	3.614	16.63	2	29	0.22
6	389	0.35	1.1	4.2	8.33	26.19	2	78	0.32
7	582	0.73	1.93	5.0	14.6	38.60	2	52	0.38
8	360	0.69	2.64	9.1	7.58	29.01	2	51	0.26
PART 2									
9	431	0.41	1.13	4.2	9.76	26.90	2	34	0.36
10	200	1.04	4.32	12.6	8.25	34.29	2	42	0.24
11	579	0.9	1.99	6.2	14.47	31.99	2	49	0.45
12	351	2.17	6.46	8.3	26.14	77.83	1	53	0.34
13	424	1.93	5.39	13.6	14.22	39.72	1	31	0.36
14	205	0.031	0.16	9.0	0.34	1.78	2	20	0.19
15	656	1.33	3.63	12.0	11.08	30.25	1	42	0.37
16	124	0.218	1.74	4.7	4.60	36.62	1	53	0.13

IV. Results for the 16 runs of the experimental design

Response variable	β_0	T β_{x_1}	NaOH β_{x_2}	Co/Fe β_{x_3}	c(Fe) β_{x_4}	M/OH β_{x_5}	m(pulp) β_{x_6}
$Y_1 = H_c$	369	-120	70	24	9	-13	34
$Y_2 = M_r$	0.82	-0.05	0.25	-0.13	-0.01	0.05	0.29
$Y_3 = M_s$	2.57	0.14	0.64	-0.32	0.08	0.001	0.87
$Y_4 = \text{Ash}$	7.96	-0.44	-0.64	0.28	1.88	0.55	1.75
$Y_5 = M_{r,\text{ash}}$	10.34	-0.88	4.24	-2.30	-1.63	-0.13	1.86
$Y_6 = M_{s,\text{ash}}$	31.95	1.71	11.7	-4.60	-4.50	-2.52	4.94
$Y_7 = \text{Peaks}$	1.50	0.00	-0.125	0.125	0.125	0.00	-0.125
$Y_8 = d_{311}$	44.31	5.56	4.56	0.19	-5.94	-1.81	1.94
$Y_9 = \text{Sq}$	0.296	-0.059	0.037	-0.018	-0.002	-0.001	0.027

V. Calculated coefficients for models of the nine response variables

RESULTS AND DISCUSSION

Table IV shows the values of the responses measured in each experiment of the experimental plan. The calculated β for all of the models are listed in Table V. As an example, the influence of the six independent variables over the numbers of peaks in the first derivative of the hysteresis curve measured on the magnetic paper (Y_7) can be expressed by the following equation:

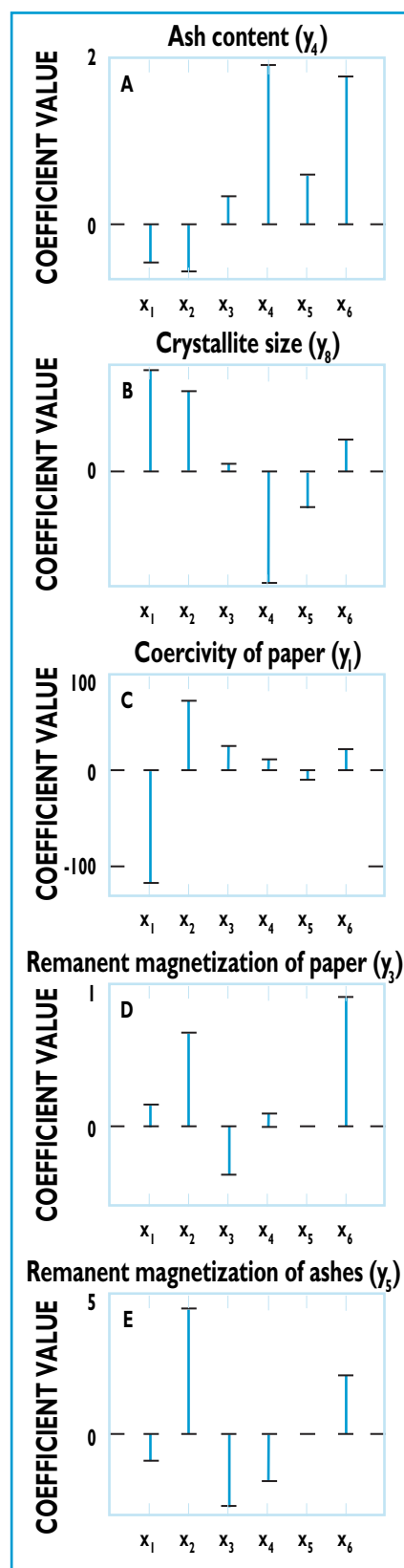
$$Y_7 = 1.5 - 0.125 \cdot X_2 + 0.125 \cdot X_3 + 0.125 \cdot X_4 - 0.125 \cdot X_6$$

This model shows that neither the synthesis temperature (X_1) nor the molar ratio M/OH (X_5) have a statistically important effect in the number of peaks. The presence of only one maximum is favored when using low initial concentrations of Fe^{2+} (X_4) and low Co/Fe ratios (X_3). The addition of NaOH in solution (X_2) also favors formation of only one peak. With the pulp at its lower level (0.8 g), the washing eliminates a great part of the ferrite crystalline particles, but the particles that cause the second peak in the derivative curve are usually larger than 0.25 mm. Therefore, the glassy particles remain with the pulp and can be detected easily.

The predictions of the mathematical equation were observed qualitatively when the syntheses were done. For example, the temperature of synthesis had no effect on the

number of peaks in the first derivative of the magnetization curve. One or two peaks were observed regardless of whether the synthesis was made at the minimum temperature of 40°C or the maximum of 90°C. The two-peak problem occurred when Co replaced some iron in the process and when the NaOH was added as pellets. The formation of the glassy particles that cause the second peak is a supersaturation problem that can be avoided by lowering the ionic concentrations either globally (using lower initial concentrations) or locally (not adding the alkali as solid pellets). Such coincidences between the mathematical results and the practical observations confirm the validity of the model.

The relative importance of the variables in the different response models can be depicted graphically, as seen in Fig. 2. For instance, to maximize ash content, the model shows that it is important to use high concentrations of iron (X_4), as seen in Fig. 2a. It is also important to use a high pulp concentration (X_6) during the synthesis, because the *in situ*-formed particles grow on the fiber walls. The third important variable is the coefficient of X_5 , which indicates that a high M/OH ratio (low amount of alkali) is favorable. This can be understood by taking into account the electrokinetic properties of the fiber-ferrite system: Both dispersed phases acquire opposite surface charges in acidic aqueous suspen-



2. Graphical representation of calculated coefficients for five response variables: Y_4 , Y_6 , Y_1 , Y_3 , and Y_5

Synthesis temperature	65°C
Suspension volume	1 L
Mass of paper pulp	10 g
$c(M^{2+})$	0.026 mole/L
Co/Fe ratio	0.5
Addition of NaOH	aqueous

VI. Reaction conditions for preparation of paper sample

H_c	707 oersted
M_r	1.17 emu/g
M_s	2.24 emu/g
$M_{r,ash}$	36.0 emu/g
$M_{s,ash}$	68.9 emu/g
d_{311}	60 nm
Peaks	1
$Sq = M_r/M_s$	0.52
Ash	3.3 wt.%

VII. Parameters measured on paper sample prepared using conditions depicted in Table VI

sions. The subsequent electrostatic attraction facilitates adsorption of the particles into the lumen walls during the impregnation step. The β_{x_2} for this model should be analyzed carefully. Its negative sign suggests that it would be preferable to add the NaOH as a solid. However, as noted previously, that contributes directly to the formation of undesir-

able large particles that stay with the fibers, elevating the ash content of the paper while diminishing its mechanical and magnetic properties.

The influence of temperature (X_1) is very interesting. It has a positive and relatively important coefficient only in the equation for the crystallite size (Y_8). Thus high synthesis temperatures are not needed to improve the measured parameters unless larger crystallites are desired. This circumstance could imply a significant energy saving at the industrial level.

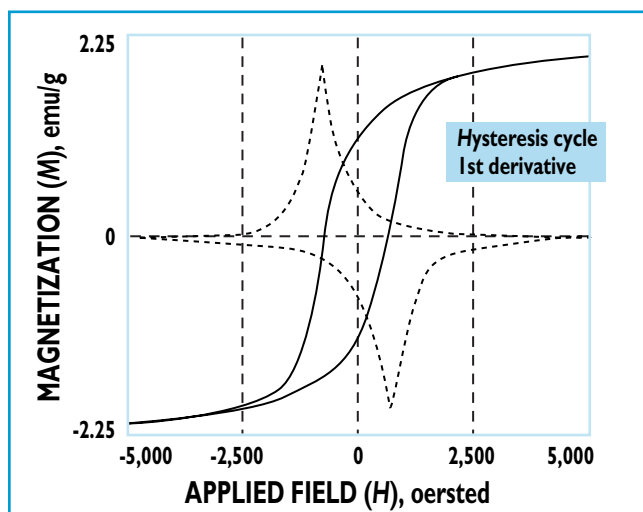
The complexity of the magnetism-related phenomena is reflected in the models obtained for the magnetic responses. An important common feature is the importance of working with high pulp concentration (X_6). Improving ferrite-inherent properties by adding more cellulose fibers to the system is not a trivial solution. The pulp influences on M_r and M_s decrease if the magnetization is referred not to the mass of paper but to the mass of ashes. (Compare the β_{x_6} values for Y_2 and Y_5 , and for Y_3 and Y_6 in Table V, or compare X_6 in Figs. 2d and 2e.) These results can be interpreted to be indicative of the

To test the indications from the model, a paper sample was prepared. Table VI lists the reaction conditions, and Table VII shows the properties of this paper. For the entire reaction time, pH was controlled to above pH 10 with additions of $\text{NaOH}_{(aq)}$. The low ash content reflects that the alkalinity of the suspension affects the impregnation level. However, this difficulty can be overcome by performing the synthesis at basic pH and the impregnation step in acid medium. Figure 3 shows the details of the magnetization curve for this paper. All magnetic parameters are comparable with that of a floppy disk (Fig. 1), which serves as a typical standard in magnetic recording.

CONCLUSIONS

Mathematical models were obtained for paper pulp magnetized by *in situ* synthesis of cobalt ferrite. According to the models, high coercivity (H_c) pulps can be prepared by conducting the reaction in alkaline medium with high pulp concentration, high ferrous ion concentration, and high Co/Fe ratio. Higher H_c values in paper are also obtained by adding the NaOH in aqueous solution (in contrast to the initial concept of adding NaOH in pellet form). These conditions also improve remanent magnetization (M_r), saturation magnetization (M_s), the squareness of the hysteresis cycle (Sq), and the crystallite size of the ferrite particles (d_{311}). The use of aqueous NaOH prevents the formation of large, poorly crystallized particles that appear when alkali is added as a solid in the presence of high concentrations of iron and cobalt. Incorporation of magnetic material into the fiber lumen is more efficient in an acidic pH range.

The only modeled parameter for which temperature has a positive and comparatively important coefficient is the average crystallite size (d_{311}). Elevated temperature did not



3. Hysteresis cycle for sample paper (Note: magnetization scale is referred to the magnetic-particle mass, which is determined by the ash content of the sample)

particular importance of the *in situ*-formed ferrite on the paper magnetic properties. The more pulp that is available for associating M^{2+} ions, which later promote formation of particles directly linked to the cellulose chains, the better will be the magnetic characteristics of the paper.

improve any of the magnetic properties nor did it increase adsorption of ferrite particles. Higher pulp concentrations had a positive influence on all the magnetic properties, indicating that the particles formed during the *in situ* synthesis step play an important role in determining the performance of magnetic papers.

The validity of the models developed in this work was confirmed by using insights gained from the model to prepare paper samples with improved magnetic properties. **TJ**

Carrazana Garcia and López Quintela are professors, Universidad de Santiago de Compostela, Facultad de Química, Departamento de Química Física, Santiago 15706, Spain.

This investigation was financed by the Xunta de Galicia (project XUGA 2090B95) and through a doctoral fellowship at the Instituto de Cooperación Iberoamericano. The authors are grateful for the help of Mayra Morales and Juan M. Lema Rodicio in their critical analysis of the manuscript.

Received for review May 1, 1998.

Accepted Nov. 13, 1998.

LITERATURE CITED

1. Nicolucci, C., European pat. 0306639 (1989).
2. Marchessault, R. H., Rioux, P., and Ricard, S., U.S. pat. 5,143,583 (1992).
3. Chagnon, M. and Hamilton, T., *J. Appl. Phys.* 67(9): 5860(1990).
4. Ebbs, G., *New Scientist* 136(1844): 22(1992).
5. Kondo, M., Japanese pat. 200,000 (1985).
6. Carrazana Garcia, J. A., López Quintela, M. A., and Rivas, J., *IEEE Trans. Magn.* 31(6): 3126(1995).
7. Malassis, M., Zagnazi, H., Poix, P., et al., *J. Matl. Sci.* 27: 876(1992).
8. Box, G. E. P. and Hunter, W. G., "Estadística para investigadores: introducción al diseño de experimentos, análisis de datos y construcción de modelos," Reverté S.A., Barcelona, 1991.
9. López Planes, R., *Diseño Estadístico de Experimentos*, Científico Técnica, La Habana, 1988, pp. 103–155.
10. Raymond, L., Revol, J.-F., Ryan, D. H., et al., *Chem. Matl.* 6: 249(1994).
11. Marchessault, R. H., Rioux, P., and Raymond, L., *Polymer* 33(19): 4024(1992).
12. "Software for automated powder diffraction," ver. 3.5b, 4th edn., Nederlandse Philips Bedrijven, IE Systems Div., Almelo, Netherlands, 1992.
13. Carrazana Garcia, J. A., López Quintela, M. A., and Rivas, J., *Colloids Surfaces A* 121: 61(1997).