

## CHEMICAL IMPREGNATION AND SINTER CORROSION IN PLAQUES FOR NICKEL-CADMIUM CELLS

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(Received February 6, 1989)

### Summary

We propose a model of the chemical impregnation of sintered plaques which makes it possible to compute the number of impregnation cycles needed to obtain the required active material loading. The active material loading influences both cell capacity and cycle life.

The model also allows the determination of the required degree of sinter corrosion during the impregnation process, and the amount of nickel in the negative active material. This nickel content influences the voltage depression in the cell discharge curve.

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### Introduction

Nickel-cadmium cells are used as power sources which can be repeatedly charged and discharged over many cycles. The electrodes for nickel-cadmium cells are usually sintered. A perforated metal screen is coated with dendritic nickel as a loose powder or as a slurry. It is then sintered at a temperature between 850 °C and 1050 °C, in an inert environment, to obtain a spongy structure containing 80% - 85% free pores [1, 2].

During the impregnation process, the active material is forced into the sinter pores: nickel hydroxide,  $\text{Ni}(\text{OH})_2$ , for the positive electrode, and cadmium hydroxide,  $\text{Cd}(\text{OH})_2$ , for the negative electrode [3, 4]. The quantity of active material in the electrodes has a significant effect on the cell performance. When the quantity of active material is too high, the cell life expectancy is reduced. The positive electrode swells, resulting in mechanical destruction of the sinter and an increase in free volume. The additional free volume absorbs electrolyte and causes the separator between the electrodes to become dry. The resulting effects are high cell resistance, reduced cell voltage, and reduced cell capacity [4 - 9]. On the other hand, when the

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quantity of active material is too low, both discharge voltage and cell capacity are reduced. It is therefore important to control the quantity of active material for optimum cell life and performance.

### Sinter corrosion

The corrosion of the nickel sinter during the impregnation process is influenced by the nature of the sintered surface, the impregnation solution, and the operating and drying conditions [10, 11]. The impregnation solution for activating the sinter surface in order to obtain good adhesion of the active material is generally acidic. The degree of acidity, the temperature, and the nitrate concentration with regard to saturation, increase the corrosion of the sinter, which is typically from 3% to 40% of the sinter weight. This tends to reduce the mechanical strength of the sinter, thereby reducing the cell life.

The positive active material produced by corrosion is less efficient than the active material produced by impregnation, possibly because it is more dense and does not permit ready access for the electrolyte.

In the negative electrode, the products of the nickel corrosion combined with the negative active material form a cadmium-nickel alloy which causes voltage depression of the cell discharge curve [12, 13]. Nickel is necessary in the active material of the negative electrode, to provide good adhesion of the active material to the sinter and to improve the recombination of oxygen when the cell is overcharged [14]. The optimum concentration of nickel is between 2 and 7 percent. of the negative active material. For this reason, it is important to control the corrosion of the sinter in the impregnation process.

The nickel corrosion rate is proportional to the surface area of the sinter, which is proportional to the sinter weight. During corrosion, the nickel in the sinter eventually becomes nickel hydroxide (*i.e.*, positive active material). The added weight caused by corrosion of the sinter during impregnation results from the addition of the hydroxyl ions and bonded water.

During the first impregnation cycle the corrosion rate will be:

$$-dm_{s1}/dt = km_{s1} \text{ with } m_{s1} = m_0 \text{ for } t = 0 \quad (1)$$

The weight of the corroded nickel is obtained by solving eqn. (1) for  $m_{s1}(t)$  and subtracting the result from the initial weight  $m_0$ :

$$m_{c1} = m_0(1 - \exp(-kt)) \quad (2)$$

A correlation coefficient of  $-0.997$  was obtained between eqn. (2) with  $k = 0.00406 \text{ min}^{-1}$  and Baumgartner's data [10]. Both are shown in Fig. 1. The factors  $0.0569 \text{ nickel ratio g}^{-1} \text{ Ni(OH)}_2$  and  $0.01363 \text{ nickel ratio mol}^{-1} \text{ NH}_3$  convert the data to the same base. With each impregnation cycle, the metallic surface available for corrosion is reduced by the hydroxide

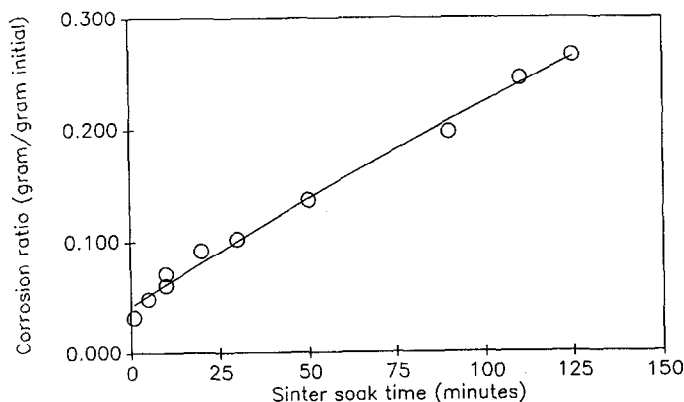


Fig. 1. Sinter corrosion und soak time.  $\circ$ , Baumgartner's data Figs. 2 and 4; —, prediction from model.

coating. Assuming this reduction to be a constant fraction of the surface available before the coating, the corrosion rate during the  $n$ th cycle will be:

$$-dm_{sn}/dt_n = k_n m_{sn} \text{ where } k_n = kf^{n-1} \text{ and } t_n = nt_1 \quad (3)$$

with initial conditions given by

$$m_{s1} = m_0 \text{ for } t = 0 \text{ and } m_{sn} = m_{s_{n-1}} \text{ for } t = t_{n-1}$$

The solution of eqn. (3) results in the weight of corroded nickel:

$$m_{cn} = m_0 - m_{sn} = m_0(1 - \exp(-ktF_n)) \quad (4)$$

where

$$F_n = \sum if^{i-1} = \sum df^i/df = d(\sum f^i)/df = (1 - f^n(1 + n - nf))/(1 - f)^2 \quad (5)$$

and the summation is done over  $i = 1$  to  $n$ .

The weight of the corroded nickel per cycle is given by:

$$\begin{aligned} m_{ccn} &= m_{n-1} - m_n = m_{n-1}(1 - \exp(-k_n nt)) \\ &= m_0 \exp(-ktF_{n-1})(1 - \exp(-k_n nt)) \end{aligned} \quad (6)$$

The corrosion rate per cycle is obtained by differentiation:

$$dm_n/dt = m_0 knf^{n-1} \exp(-ktF_n) \quad (7)$$

and is plotted in Fig. 2 with Baumgartner [10] data with  $f = 0.48$ .

### Weight gain during impregnation

The impregnation process is performed by immersing the sintered plate in an aqueous solution of a nitrate salt and converting the nitrate to a hydroxide by drying and soaking in sodium hydroxide [2].

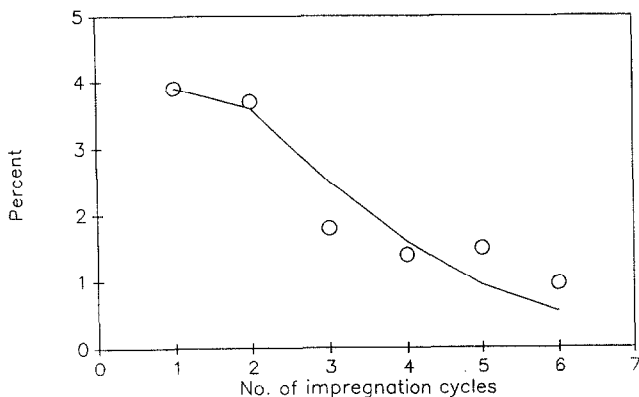
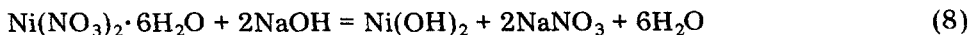


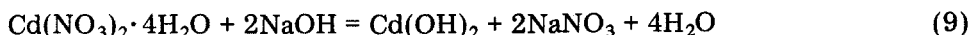
Fig. 2. Corrosion per cycle. Points from Baumgartner's data Table 3. —, Prediction from model.

The following chemical reactions occur in the process:

For the positive impregnation:



and for the negative impregnation:



The nickel and cadmium hydroxides are not soluble in the basic solution and precipitate in the pores of the sinter. Normally, four to eight such soak cycles are performed to obtain the required amount of active material in the electrode.

The following model for weight gain in the impregnation process is based on a volume balance in the sinter pores. In each of the impregnation cycles, the nitrate salt solution fills most of the free volume. For a given solution composition and impregnation temperature,  $R$ , the ratio between the active material volume and the free volume is independent of the impregnation cycle. The weight of active material per unit solution volume is given as:

$$R_d = C_s M_{\text{Oh}} / M \quad (10)$$

The added weight of the active material in each impregnation cycle consists of the sum of three contributions. First, the gain by the solution, which fills a portion,  $b$ , of the total pore volume available. Second, the weight gain of hydroxide,  $(\text{OH})_2$ , due to corrosion of the sinter. Third, the weight gain due to surface deposit (later to be removed by brushing). Thus the first impregnation cycle weight gain is given by:

$$m_1 = V_0(R_d b + K_0 m_{\text{cc1}} / m_0) + A_{s1} \quad (11)$$

where:

$$K_0 = (1 - P)M_h d_N / (PM_N) \quad (12)$$

Similarly, the weight gain in the  $n$ th impregnation cycle is given by:

$$m_n = V_0 R_d b (1 - R)^{n-1} U_n + A_{s_n} \quad (13)$$

where:

$$U_n = 1 + K_0 m_{ccn} (1 - R)^{1-n} / (R_d b) - K_h K_0 \sum m_{cc(i-1)} (1 - R)^{-(i-1)} \quad (14)$$

and the summation is done for  $i = 1$  to  $n$ . The apparent hydroxide specific volume,  $K_h$ , is given by:

$$K_h = M_N / (M_h d_{oh}) - 1 / d_N \quad (15)$$

$U_n$  is the sinter corrosion factor which, for no corrosion, is equal to unity. The second term in  $U_n$  is the added volume ratio due to corrosion, and the third term results from the reduction in the void volume due to corrosion products.

## Experimental

The following data, obtained experimentally as well as from production line measurements, validates the models. Positive and negative plaques for nickel-cadmium cells, with total areas of 869 and 1042 cm<sup>2</sup>, respectively, were produced by nickel powder from nickel carbonyl spread on a nickel-plated-steel substrate weighing 0.032 g cm<sup>-2</sup>. The resulting sintered plaques had a porosity of 83.5 ± 1.5% and an average thickness of 0.090 cm for positive and 0.094 cm for negative plaques. The sintered plaques were chemically impregnated in a nitrate solution, dried, and the nitrate converted to hydroxide by dipping in a caustic solution. The plaques were then washed with water and re-dried. The nitrate solution contained 1.363 g ml<sup>-1</sup> Ni(NO<sub>3</sub>)·6H<sub>2</sub>O for the positive-, and 1.432 g ml<sup>-1</sup> Cd(NO<sub>3</sub>)·5H<sub>2</sub>O for the negative impregnation. Several such impregnation cycles were performed and the plaques were weighed after each cycle to an accuracy of ±0.5 g.

The various variables were calculated from the production impregnation of positive and negative plaques, with input data according to Table 1. The weight gains on each cycle are the averages of 10 plaques.  $R_d$ ,  $K_0$ ,  $K_h$  were calculated from eqns. (10), (12), (15). Then,  $kt$  was evaluated from eqns. (2) and (11). The resulting model for weight gain during impregnation (eqn. (13)) requires three additional parameters:  $R$ ,  $b$  and  $f$ . These parameters were evaluated by fitting the data to the model.

Since  $U_n$  changes only moderately with the number of cycles, except for the first one when corrosion is greatest, a logarithmic regression was performed on weight gain *versus* cycle number for cycles 2 - 6. The high correlation coefficient of -0.993 to -0.997, obtained by the regression, indicates that  $U_a$ , which is the average of  $U_n$ , can be used for all cycles except the first. Thus, following eqn. (13) and the logarithmic regression:

$$\ln(m_n - A_{s_n}) = a + cn \quad n \geq 2 \quad (16)$$

TABLE 1  
Impregnation data

Symbol	Units	Batch 1 Positive	Batch 2 Positive	Batch 3 Negative	Batch 4 Negative
$A_s$	g	0.6	0.6	0.75	0.75
$C_s$	$\text{g cm}^{-3}$	1.363	1.363	1.432	1.432
$V_0$	$\text{cm}^3$	49.9	48.8	57.0	58.7
$P$	—	0.835	0.835	0.835	0.835
$d$	$\text{g cm}^{-3}$	3.53	3.53	4.79	4.79
$d_N$	$\text{g cm}^{-3}$	8.9	8.9	8.9	8.9
$d_{oh}$	$\text{g cm}^{-3}$	3.53	3.53	3.53	3.53
$M$	$\text{g mol}^{-1}$	290.79	290.79	308.48	308.48
$M_h$	$\text{g mol}^{-1}$	52	52	52	52
$M_N$	$\text{g mol}^{-1}$	58.7	58.7	58.7	58.7
$M_{oh}$	$\text{g mol}^{-1}$	92.7	92.7	164.4	164.4
$m_1$	g	27.1	23.1	43.0	45.9
$m_2$	g	15.9	16.8	34.0	34.8
$m_3$	g	14.2	14.1	22.1	27.1
$m_4$	g	12.1	12.9	18.2	18.8
$m_5$	g	10.1	10.2	13.2	14.9
$m_6$	g	9.0	8.9	9.1	9.9

Resulting in:

$$R = 1 - \exp(c) \quad (17)$$

The corrosion factor ( $f$ ) and the fill ratio ( $b$ ) were calculated by a trial and error procedure so that the correlated  $U_a$  matches the calculated one and there is a minimum deviation between data and calculated values.

$$U_a = \exp(a)/(V_0 R_d b) \quad (18)$$

$$\text{Er} = \min. \sum (m_{n\text{data}} - m_{n\text{model}})^2 \quad (19)$$

The parameters  $f$  and  $b$  should therefore simultaneously satisfy eqns. (18) and (19).

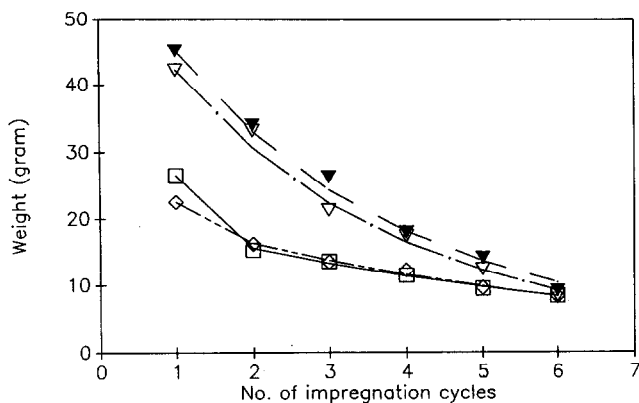
Calculated results for the four impregnation batches in which the process was performed under different conditions are given in Table 2 and shown in Figs. 3 and 4. Batches 1 and 4 were from highly corroded plaques and batches 2 and 3 were from controlled impregnation conditions which yield cells having good performance. The good agreement between model and experimental data is apparent.

## Discussion

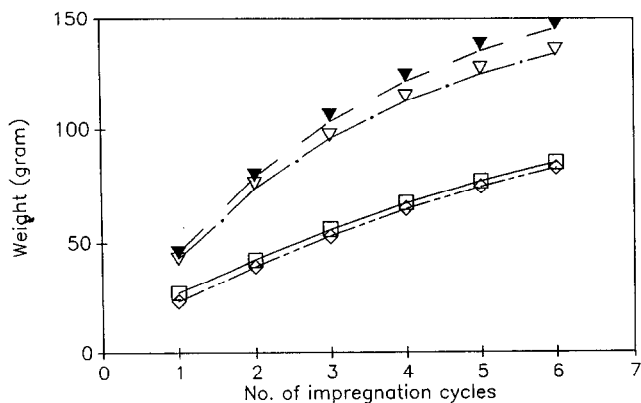
The coefficients in Table 2 show that batches 1 and 4 have high nickel sinter corrosion. With such a corrosion rate the sinter becomes weak, causing

**TABLE 2**  
Calculated coefficients

Symbol	Units	Batch 1 Positive	Batch 2 Positive	Batch 3 Negative	Batch 4 Negative
$b$	—	0.870	0.918	0.964	0.998
$f$	—	0.001	0.01	0.99	0.99
$kt$	—	0.103	0.0408	0.0034	0.0047
$K_h$	$\text{cm}^3 \text{g}^{-1}$	0.207	0.207	0.207	0.207
$K_0$	$\text{g cm}^{-3}$	1.558	1.558	1.558	1.558
$R$	—	0.144	0.155	0.281	0.277
$R_d$	$\text{g cm}^{-3}$	0.434	0.434	0.763	0.763



**Fig. 3.** Weight gain per cycle. Positive: — and - - -, model;  $\square$  and  $\diamond$ , production data; negative: - - - and - · -, model;  $\nabla$  and  $\blacktriangledown$ , production data.



**Fig. 4.** Total weight gain. Positive: — and - - -, model;  $\square$  and  $\diamond$ , production data; negative: - - - and - · -, model;  $\nabla$  and  $\blacktriangledown$ , production data.

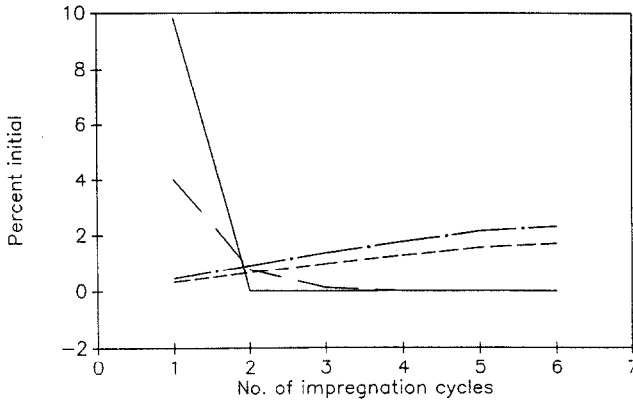


Fig. 5. Sinter corrosion per cycle, prediction from model. — and — — —, positive; - . - and . . . , negative.

plate disintegration in the cell. For the positive batches, the corrosion is high during the first impregnation cycle and practically non-existent on successive cycles (Fig. 5). It suggests that the nickel hydroxide  $(\text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O})$  produced by corrosion, forms a compact layer which prevents further corrosion in successive cycles. On the other hand, the negative batches have a low initial corrosion rate, leaving a permeable nickel hydroxide layer, and therefore the corrosion rate is not reduced appreciably with impregnation cycles.

Further impregnation parameters which are not apparent initially from the weight gain data, can be calculated by the model. These are:  
The % nickel corroded from the sinter:

$$N_c = 100m_{cn}/m_0 = 100(1 - \exp(-ktF_n)) \quad (20)$$

The % of nickel in negative active material:

$$N_a = W_{hn}M_N/(M_h W_n) \quad (21)$$

where the weight increase due to corrosion is:

$$W_{hn} = V_0 K_0 m_{cn}/m_0 = V_0 K_0 (1 - \exp(-ktF_n)) \quad (22)$$

and the total weight gain:

$$W_n = \sum m_i \quad i = 1 \text{ to } n \quad (23)$$

Some of the results are shown in Table 3.

The total weight gain as a function of the impregnation cycle, together with the model prediction for positive and negative plaques is shown in Table 3 and previously in Fig. 4. This weight gain is not entirely due to active material, and can therefore lead to an error in the calculated capacity and the balance of the positive to negative ratio. The net active material is obtained from the model and the following relations:



TABLE 3

Calculated impregnation parameters

Symbol	Units	Batch 1 Positive	Batch 2 Positive	Batch 3 Negative	Batch 4 Negative
$N_c$	%	9.8	4.9	6.6	9.1
$N_a$	%	—	—	5.0	6.5
$N_v$	%	40.6	47.6	48.9	45.7
$W_6$	g	88.4	86.0	139.6	151.4
$W_{a6}$	g	93.4	86.6	129.2	138.5

For the positive:

$$W_{an} = W_n + W_{hn}M_N/M_h \quad (24)$$

For the negative:

$$W_{an} = W_n - W_{hn} \quad (25)$$

Figure 6 shows the active material weight evaluated from eqns. (24) and (25). These equations can therefore be used to determine the required number of impregnation cycles for a specific active material loading.

The free volume remaining after impregnation is an important factor in the determination of the amount of electrolyte needed for a specific cell design and active material loading. The % free volume after impregnation to sinter volume can be calculated from:

$$N_v = 100(1 - W_a/(dV_0) - V_c) \quad (26)$$

where the volume due to corrosion products is:

$$V_c = K_0K_h m_{cn}/m_0 \quad (27)$$

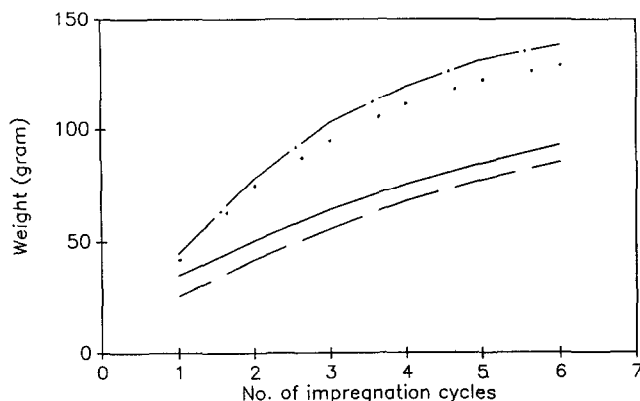


Fig. 6. Total active material, prediction from model. — and ---, positive; · · · and - · - ·, negative.

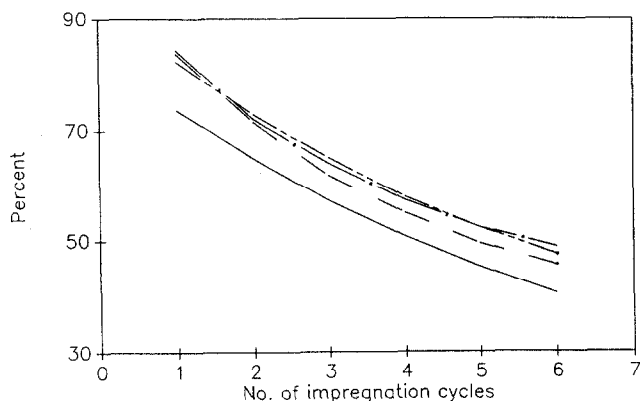


Fig. 7. Free to sinter void volume, prediction from model. Positive, — and - - - -; negative, - - - and - . - .

The ratio of free to sinter volume for the four batches is shown in Fig. 7. This ratio is about 6% lower for batch 1 due to greater corrosion.

### List of symbols

$a$	Intercept of correlation
$A_s$	Weight gain outside pores per cycle (g)
$b$	Solution filling volume per free volume
$c$	Slope of correlation
$C_s$	Solution concentration; weight nitrate salt per solution volume ( $\text{g cm}^{-3}$ )
$d$	Density of active material ( $\text{g cm}^{-3}$ )
$d_N$	Density of nickel ( $\text{g cm}^{-3}$ )
$d_{\text{oh}}$	Density of nickel hydroxide ( $\text{g cm}^{-3}$ )
$E_r$	Square of difference between data and model weight gain ( $\text{g}^2$ )
$f_n$	Corrosion reduction factor on cycle $n$
$F_n$	Total corrosion reduction factor up to cycle $n$
$k$	Corrosion rate constant on first impregnation cycle ( $\text{l min}^{-1}$ )
$k_n$	Corrosion rate constant on $n$ impregnation cycle ( $\text{l min}^{-1}$ )
$K_0$	Weight of nickel sinter (as hydroxide) per void volume ( $\text{g cm}^{-3}$ )
$K_h$	Hydroxide volume per unit weight ( $\text{cm}^3 \text{g}^{-1}$ )
$m_1$	Added weight in first cycle of impregnation (g)
$m_{c1}$	Weight of corroded nickel after first impregnation cycle (g)
$m_{cn}$	Weight of corroded nickel on $n$ impregnation cycle (g)
$m_{cn}$	Weight of corroded nickel after $n$ impregnation cycles (g)
$m_n$	Added weight on $n$ cycle of impregnation (g)
$m_0$	Initial amount of nickel sinter (g)
$m_{s1}$	Weight of nickel sinter after first impregnation cycle (g)
$m_{sn}$	Weight of nickel sinter after $n$ impregnation cycles (g)

$M$	Molecular weight of nitrate salt ( $\text{g mol}^{-1}$ )
$M_N$	Molecular weight of nickel ( $\text{g mol}^{-1}$ )
$M_{\text{oh}}$	Molecular weight of active material ( $\text{g mol}^{-1}$ )
$M_h$	Molecular weight of $(\text{OH})_2\text{H}_2\text{O}$ ( $\text{g mol}^{-1}$ )
$n$	Number of impregnation cycles
$N_a$	Nickel in negative active material (%)
$N_c$	Nickel corroded from sinter (%)
$N_v$	Free volume to sinter void volume (%)
$P$	Porosity of sinter in active area; void volume per total sinter volume
$R$	Ratio of active material volume to sinter void volume
$R_d$	Active material weight to solution volume ( $\text{g cm}^{-3}$ )
$S$	Total plaque area ( $\text{cm}^2$ )
$t$	Equivalent impregnation time per cycle (min)
$t_n$	Equivalent impregnation time after $n$ cycles (min)
$U_a$	Average corrosion gain factor
$U_n$	Corrosion gain factor on $n$ cycle
$V_0$	Void volume of sintered plaque ( $\text{cm}^3$ )
$W_{an}$	Active material weight gain after $n$ impregnation cycles (g)
$W_{hn}$	Weight increase due to corrosion after $n$ cycles (g)
$W_n$	Weight gain after $n$ cycles of impregnation (g)

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