

# Optimizing Recycling Processes for Mixed LFP/NMC Lithium-Ion Batteries: A Comparative Study of Acid-Excess and Acid-Deficient Leaching

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**Table S1.** F-values and p-values for each effect, interactions between effect and quadratic effects of an acid-excess leaching (bold: effects taken into consideration in the DoE model).

	Ni		Mn		Co	
Source	F-value	p-value	F-value	p-value	F-value	p-value
H <sub>2</sub> SO <sub>4</sub>	0,0552	0,8210	0,2671	0,6212	0,0811	0,7841
H <sub>2</sub> O <sub>2</sub>	92,1412	<0,0001	75,4394	<0,0001	70,5040	<0,0001
S/L	100,4724	<0,0001	33,1595	0,0007	33,2221	0,0007
H <sub>2</sub> SO <sub>4</sub> * H <sub>2</sub> O <sub>2</sub>	3,6111	0,0992	1,7397	0,2287	1,6843	0,2355
H <sub>2</sub> SO <sub>4</sub> *S/L	0,1395	0,7198	0,0172	0,8994	0,0128	0,9131
H <sub>2</sub> O <sub>2</sub> *S/L	13,0010	0,0087	11,5864	0,0114	11,4268	0,0118
H <sub>2</sub> SO <sub>4</sub> * H <sub>2</sub> SO <sub>4</sub>	2,0463	0,1957	0,1982	0,6696	0,0908	0,7720
H <sub>2</sub> O <sub>2</sub> * H <sub>2</sub> O <sub>2</sub>	0,0483	0,8324	0,0008	0,9781	0,0417	0,8440
S/L*S/L	0,0483	0,8324	1,3039	0,2911	2,3402	0,1699

**Table S2.** Threshold F-values from the Fisher-Snedecor table for different degrees of freedom (df1=(number of parameters-1), df2=(number of tests-1), significance level  $\alpha=0.05$ ).

df1 \ df2	1	2	3	4	5	6	7	8	9	10
1	161.45	199.50	215.71	224.58	230.16	233.99	236.77	238.88	240.54	241.88
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35

The quality of the DoE has been evaluated by using the following statistical indicators:

F-values

$$F - value = \frac{\sum_{i=1}^k n_i (\bar{x}_i - \bar{X})^2}{k - 1} \bigg/ \frac{\sum_{i=1}^k \sum_{j=1}^{n_i} (x_{ij} - \bar{x}_i)^2}{N - k}$$

where  $k$  is the number of groups ( $k-1$  is the degree of freedom),  $n_i$  is the sample size of the group  $i$ ,  $\bar{x}_i$  is the mean of the group  $i$ ,  $\bar{X}$  is the grand mean,  $N$  is the total number of observations and  $x_{ij}$  is the  $j$  observation in the group  $i$ .

The MSE provides an unbiased estimate of the population variance within groups, assuming the null hypothesis is true. This number is then compared to the  $F$  threshold-value given by the Fisher-Snedecor table for specific values of  $df1=(\text{number of parameters}-1)$  and  $df2=(\text{number of tests}-1)$  for a given significance level

For acid-excess leaching,  $df1_{\text{acid-excess}}=2$  and  $df2_{\text{acid-excess}}=16$  and for acid-deficient leaching  $df1_{\text{acid-deficient}}=1$  and  $df2_{\text{acid-deficient}}=9$ . Table SI2 presents the table of Fisher-Snedecor for a significance level  $\alpha=0.05$  (probability of significance=95%). For the acid-excess leaching model, the threshold  $F$ -value is 3.63 whereas for the acid-deficient leaching, the  $F$  critical value is 5.12.

If the  $F$ -value is higher than the threshold  $F$ -value then the null-hypothesis must be rejected and no significant statistical difference between at least two groups can be expected.

$p$ -value

The  $p$ -values are reported in the table of Student. It quantifies the probability of obtaining the observed value, or more extreme results, assuming that the null-hypothesis is true. It ranges from 0 to 1, with lower values indicating stronger evidence against the null-hypothesis. Usually,  $p$ -values are lower than 0.05.

Coefficient of determination  $R^2$

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}}$$

where  $SS_{res}$  is the sum of squares of residual defined by:

$$SS_{res} = \sum (y_i - \hat{y}_i)^2 \text{ with } y_i \text{ the observed values and } \hat{y}_i \text{ are the predicted values.}$$

$SS_{tot}$  is the total sum of squares defined by:

$$SS_{tot} = \sum_{i=1}^n (y_i - \bar{y})^2$$

with  $\bar{y}$  the mean of the observed data.

$R^2$  always falls between 0 and 1 ( $R^2=1$  indicates a perfect agreement between the model and the data).

Adjusted coefficient of determination  $R_{adj}^2$

$$R_{adj}^2 = 1 - \left( \frac{(1 - R^2)(n - 1)}{n - k - 1} \right)$$

where  $n$  is the number of observations in the sample and  $k$  is the number of independent variables in the regression model.

$R^2$  decrease when non-significant predictors are added to the model.  $R_{adj}^2$  values are lower  $R^2$  or it can be equal to  $R^2$ .  $R_{adj}^2$  can also be negative, especially when  $R^2$  is close to zero. A negative  $R_{adj}^2$  means that the model is worse than a simple average of the observed value.

RMSE:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2}$$

where  $n$  is the number of observations,  $y_i$  the observed values and  $\hat{y}_i$  are the predicted values

The Root Mean Square Error (RMSE) measures the differences between calculated values and experimental values. It ranges from 0 to positive infinity, with 0 representing a perfect fit. Low RMSE values indicate better model fit and more precise predictions.

**Table S3.** Main parameters of the model variance from the prediction equations determined with JMP software for the dissolution efficiency of Ni, Mn and Co in an acid deficiency leaching.

	F-value	p-value	R <sup>2</sup>	R <sup>2</sup> adj.	RMSE
Ni	1.35	0.4292	0.69	0.18	1.24
Mn	1.41	0.4126	0.70	0.21	1.68
Co	1.17	0.4784	0.66	0.10	1.57
Li	0.83	0.5597	0.58	-0.11	0.88

**Table S4.** Theoretical dissolution yield (%D) of Ni, Mn, Co and Li after reintroduction of 60% (Wt. %) of the residue.

step of the iteration	%D <sub>Ni</sub>	%D <sub>Mn</sub>	%D <sub>Co</sub>	%D <sub>Li</sub>
0	76.7	76	76.6	80.1
1	87.42266	86.944	87.35464	89.66394
2	88.92169	88.51994	88.86459	90.80587
3	89.13125	88.74687	89.07659	90.94222
4	89.16055	88.77955	89.10635	90.95850
5	89.16464	88.78426	89.11053	90.96045
6	89.16522	88.78493	89.11112	90.96068
7	89.16530	88.78503	89.11120	90.96070
8	89.16531	88.78504	89.11121	90.96071
9	89.16531	88.78505	89.11121	90.96071
10	89.16531	88.78505	89.11121	90.96071

**Table S5.** Percentages of metals contained in the PLS obtained by acid-excess and acid-deficient leaching.

	Ni	Mn	Co	Li	Fe	Al	Cu
Acid-excess Leaching	46.2	2.8	6.3	10.2	32.0	0.7	1.9
Deficient-acid leaching with reintroduction (calculated by the mass-balance model)	68.7	4.1	9.4	17.4	0.0	0.0	0.4

**Table S6.** Concentrations of Ni, Mn, Co, Li and Cu before and after Mn extraction with DEHPA 0.5 mol.L<sup>-1</sup> in kerosene, and after scrubbing with a solution of 3g/L of Mn.

	Ni (mg/L)	Mn (mg/L)	Co (mg/L)	Li (mg/L)	Cu (mg/L)
Solution after Cyanex 272 extraction	192	735	1290	0	16.5
Solution after D2EHPA extraction	0	374	12	0	5.2

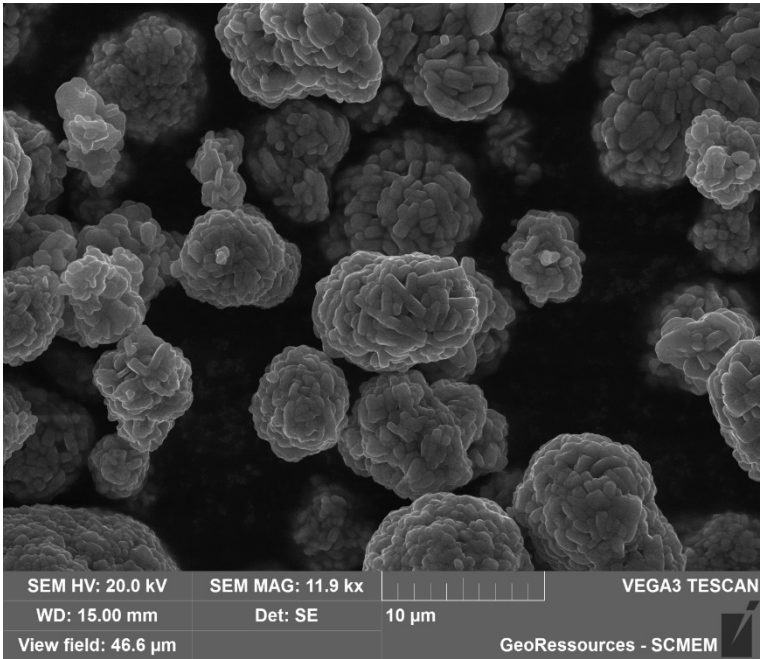
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Solution after scrubbing with a 3g/L Mn solution	0	2164	0	0	0.2
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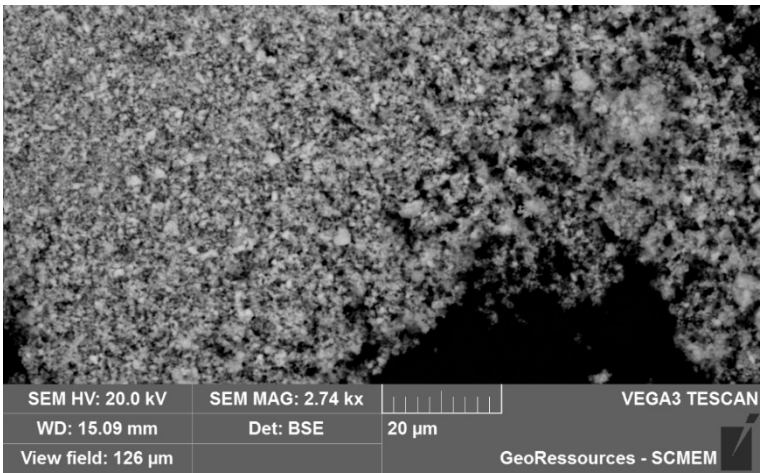
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FIGURES

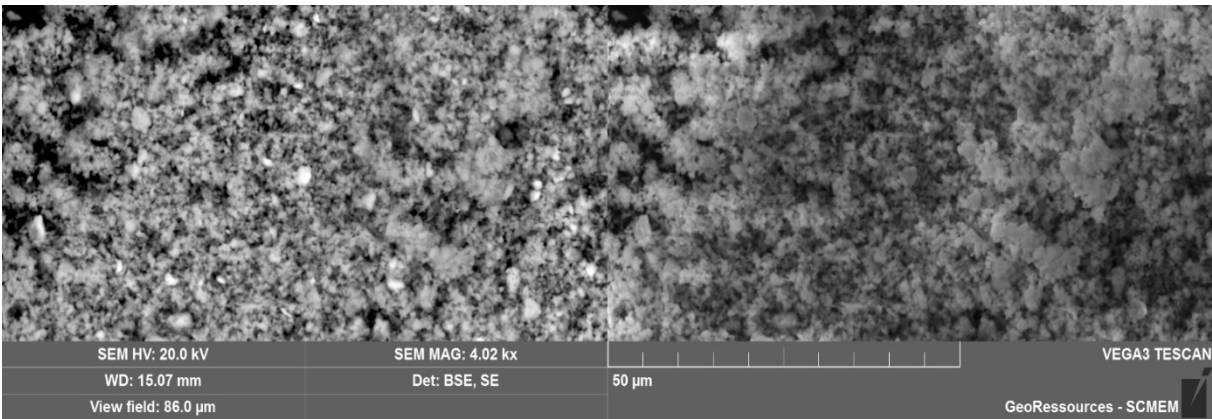
(a)



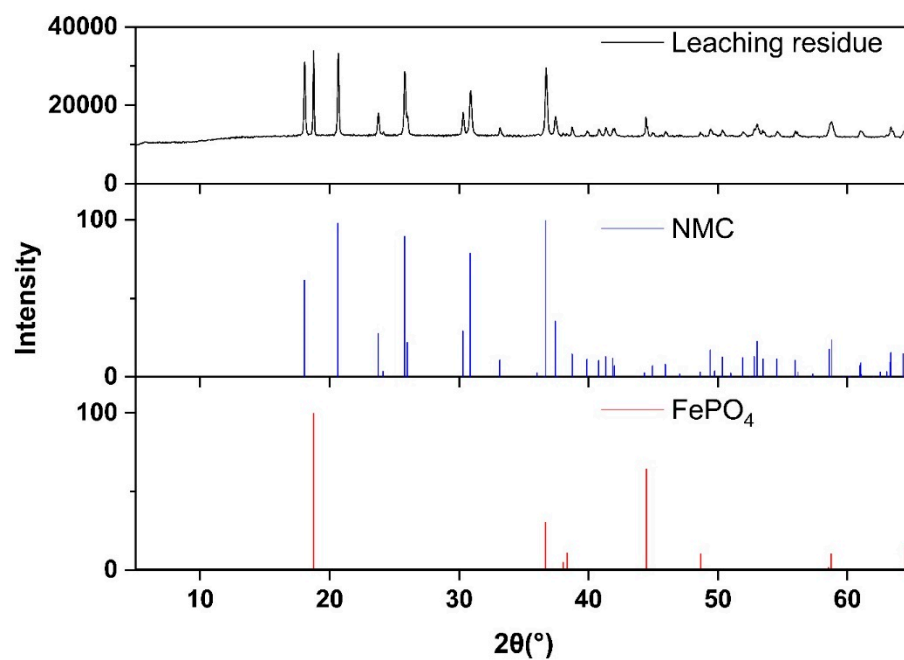
(b)



(c)



**Figure 1.** SEM picture of a particle of NMC cathode material (a), LFP cathode material (b), leaching residue after 240 min acid-deficient leaching reagent, LFP and NMC. Experimental leaching conditions: 0.4 mol/L  $\text{H}_2\text{SO}_4$  + 3% (Vol. %)  $\text{H}_2\text{O}_2$  at 30 °C and S/L=50 g/L.



**Figure S2.** XRD patterns of the leaching residue after 240 min acid-deficient leaching reagent, LFP and NMC. Experimental leaching conditions: 0.4 mol/L  $\text{H}_2\text{SO}_4$  + 3% (Vol. %)  $\text{H}_2\text{O}_2$  at 30 °C and S/L=50 g/L.