Open Journal of Applied Sciences, 2022, 12, 598-613
https://www.scirp.org/journal/ojapps
ISSN Online: 2165-3925
ISSN Print: 2165-3917

Manganese Dioxide (MnO_2) Gaining by Calcination of Manganese Carbonate ($MnCO_3$) Precipitated from Cobalt Removal Solutions

Chungu Mwana Mwamba Yannick[1], Michael Kabangu Ngoie[1], Muliangala Mbalaba Francis[1], Kasambay Mutangala Francis[1], Mulaja Tshakatumba Constantin[1], Ilunga Mutombo Gabriel[1], Ilunga Mwanza Israel[2]

[1]Department of Metallurgy and Materials, Faculty of Polytechnics/University of Lubumbashi, Lubumbashi, Democratic Republic of the Congo
[2]Laboratory of Metallography, Faculty of Polytechnics, University of Lubumbashi, Lubumbashi, Democratic Republic of the Congo
Email: kabangu.ngoie@unilu.ac.cd

How to cite this paper: Yannick, C.M.M., Ngoie, M.K., Francis, M.M., Constantin, M.T., Francis, K.M., Gabriel, I.M. and Israel, I.M. (2022) Manganese Dioxide (MnO_2) Gaining by Calcination of Manganese Carbonate ($MnCO_3$) Precipitated from Cobalt Removal Solutions. *Open Journal of Applied Sciences*, **12**, 598-613.
https://doi.org/10.4236/ojapps.2022.124041

Received: February 12, 2022
Accepted: April 26, 2022
Published: April 29, 2022

Abstract

Precipitation was carried out to obtain manganese carbonate by adding a precipitating agent, sodium carbonate ($NaCO_3$). This was followed by calcination of the manganese carbonate ($MnCO_3$) to obtain manganese dioxide (MnO_2). For precipitation tests, a pH ranging from 8 to 10, a time of one to two hours, and a temperature of 25˚C and 50˚C are the parameters that are considered. The calcination of $MnCO_3$ is carried out under the following conditions: time (1, 2, 3, and 4 hours) and temperature (370˚C, 420˚C, and 470˚C). It should be noted that the temperature range selected for the calcination tests is based on thermodynamic data obtained using the HSC CHEMISTRY software. The results obtained show an effective recovery of manganese at 25˚C, in one hour, with a pH of 8.5 with a precipitation yield and manganese content in the precipitate around 98.43% and 24.21%, respectively. During calcination tests, results show an increase in mass loss, for a constant calcination time, as temperature increases. On the other hand, increasing the calcination time at a given temperature causes an increase in mass loss. However, a significant decrease in mass loss is noted at 3 hours of calcination. The highest mass loss is obtained at a temperature of 470˚C after 4 hours of calcination.

Keywords

Manganese, Calcination Temperature, Carbonate, Manganese Dioxide, Precipitation

1. Introduction

The current energy consumption model is based almost entirely on the use of fossil fuels, including oil, natural gas, and coal: they are limited and polluting. Research is being carried out to develop renewable or alternative resources and to limit the consumption of fossil fuels. One of the fastest-growing technologies is the manufacture of batteries for electric vehicles. These batteries are made of cobalt, lithium, and manganese [1].

The aim of this research is based on the massive production of manganese dioxide, a form of manganese oxide used in the manufacture of batteries industries, particularly lithium batteries, and it is initiated as part of the key research on the use of manganese in batteries [2] and accumulators [3]. This research is based on the desire to recover the manganese currently that occurred in the production process of the hydrometallurgical plant's area. Further, it is about the manganese's recovery that occurs in sulphate solution as a carbonate, in order to obtain manganese dioxide by calcination. Based on previous experiences, chemical precipitation method has great significance in the purification process of manganese solutions. This research aims to clarify the use of carbonate as precipitants of calcium and magnesium ions [4] [5].

In Central Africa, the Copper belt region extending from DRC to Zambia contains the largest reserve of copper and cobalt ore. The standard treatment process for Copper belt ores area consists of stirred tank leaching, solvent extraction and electrowinning in order to produce high quality of copper. A bleed in the copper solvent extraction circuit is then used to produce cobalt as a precipitate (cobalt hydroxide). Removal of iron, manganese and other impurities is required in order to produce high-quality cobalt [6].

We set out ourselves the following objectives: to determine the optimal conditions in order to obtain efficient and selective recovery of the manganese present in the sulfate solution resulting from the cobalt's removal and to evaluate under which conditions it is possible to obtain manganese dioxide from the initial form which manganese is extracted from the solution.

2. Theoretical Reminder

1) Concepts of manganese carbonate precipitation

Reagent choice

It is usually very difficult to separate calcium and magnesium from manganese in sulfate solutions. This is due to their very similar chemical properties. Separation methods include chemical precipitation (such as fluoride, sulfide, hydroxide, carbonate or oxidation precipitation by SO_2/O_2 mixture) and solvent extraction.

Figure 1 that illustrated from the work of Lin [7] indicated that when pH varies from 2 to 13, the equilibrium concentration of Mn^{2+}, Mg^{2+}, and Ca^{2+} drops linearly in case of hydroxide precipitation. On the other hand, in the precipitation of carbonates, it is found that the decrease of the equilibrium concentration when pH is increased is no longer linear. In addition, we note that for a given

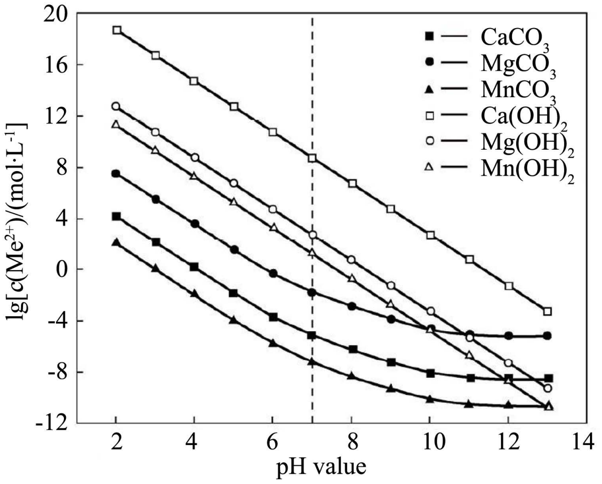


Figure 1. Concentration of Mn, Mg, Ca during the precipitation of a carbonate and a hydroxide.

pH, the precipitation potential of Mn^{2+}, Mg^{2+} and Ca^{2+} evolves as follows: $MnCO_3 > CaCO_3 > MgCO_3 > Mn(OH)_2 > Mg(OH)_2 > Ca(OH)_2$.

From a thermodynamic standpoint, carbonate precipitation is more practical for separating manganese from magnesium and calcium due to its better selectivity for manganese over magnesium. This is beneficial for obtaining a higher quality manganese precipitate from a sulfate solution with a high magnesium concentration and a low calcium concentration [8].

The precipitation of divalent metals (Me^{2+}) by addition of carbonate ions in a sulfate solution occurs according to the reaction: $Me^{2+} + CO_3^{2-} = MeCO_3 \downarrow$. In the precipitation of carbonate, it is found that precipitation yield increases with increasing pH. The precipitation indeed yield is likely to vary from 91.55% to 99.98% when pH varies from 8.5 to 10.5 [9].

Magnesium and Calcium behavior

The precipitation of manganese carbonate in the presence of calcium and magnesium is accompanied by co-precipitation of these two impurities. Calcium precipitates in the form of calcium carbonate whose composition and crystallographic variety depend on the temperature and the Mg/Ca ratio. Magnesium precipitates in the form of an anhydrous or hydrated carbonate ($MgCO_3 \cdot H_2O$; $MgCO_3 \cdot 2H_2O$; $MgCO_3 \cdot 3H_2O$; $MgCO_3 \cdot 5H_2O$) [10].

2) Calcination notion

The treated sulfate solution contains magnesium and calcium, it is expected that the resulting manganese carbonate precipitate will also contain magnesium carbonate as the main impurity as well as calcium carbonate.

Through the HSC CHEMISTRY software (version 9.5.1), it is possible to predict the temperature at which the decomposition of each carbonate present in the sample became possible. Therefore, it is possible to define a temperature range for the calcination tests. **Table 1** below shows the thermodynamic data of the calcination reactions.

Table 1. Thermodynamic data of calcination reactions.

Temperature [˚C]	Gibbs free enthalpy [kcal]			
	$MnCO_3 = MnO + CO_2$	$2MnO + O_2 = 2MnO_2$	$6MnO + O_2 = 2Mn_3O_4$	$4MnO + O_2 = 2Mn_2O_3$
0	13.603	−50.195	−94.669	−75.573
100	9.596	−44.965	−89.113	−70.264
200	5.619	−39.729	−83.533	−64.965
300	1.688	−34.522	−77.965	−59.669
400	−2.195	−29.351	−72.425	−54.392
500	−6.029	−24.214	−66.922	−49.144
600	−9.815	−19.105	−61.462	−43.937
700	−13.552	−14.014	−56.051	−38.777
800	−17.240	−8.932	−50.691	−33.673
900	−20.879	−3.848	−45.387	−28.629
1000	−24.468	1.250	−40.141	−23.65
Temperature [˚C]	**Gibbs free enthalpy [kcal]**			
	$Mn_3O_4 + O_2 = 3MnO_2$	$2Mn_2O_3 + O_2 = 4MnO_2$	$MgCO_3 = MgO + CO_2$	$CaCO_3 = CaO + CO_2$
0	−27.958	−24.817	12.649	32.13
100	−22.891	−19.665	8.457	28.313
200	−17.827	−14.493	4.293	24.543
300	−12.801	−9.375	0.172	20.824
400	−7.815	−4.311	−3.9	17.156
500	−2.861	0.715	−7.914	13.537
600	2.073	5.727	−11.866	9.965
700	7.004	10.749	−15.751	6.44
800	11.947	15.808	−19.563	2.96
900	16.922	20.932	−23.299	−0.475
1000	21.945	26.150	−26.842	−3.864

Based on the data contained in Table 1, the calculation of inversion temperatures leads to the following conclusions:

- The calcination temperature must be higher than 345.5˚C, because this is the temperature required for decomposition of manganese carbonate begins.
- The calcination temperature must be lower than 975˚C to avoid the decomposition reaction of the MnO_2 that would have been formed.
- The calcination temperature must be lower than 557.98˚C to allow the oxidation of Mn_3O_4 to form manganese dioxide.
- The calcination temperature must be lower than 486˚C to make possible the formation of manganese dioxide by oxidation of Mn_2O_3.

In conclusion, the calcination should be done between approximately 343.5˚C and 486˚C.

As for the impurities, it can be seen that the calcination of magnesium carbonate starts at 304.2˚C while that of calcium carbonate is only possible from 886.17˚C.

3. Instrumentation

1) Precipitation tests

Material and Method

The precipitation tests were conducted on a sample of the post-settling decanter overflow from the Ruashi Mining hydrometallurgical plant. It was a 40-litre mixture from two samples of 20-litre for each. The sodium carbonate used was prepared at 100 g/l.

Two samples were performed under the following conditions: pH (7.5 and 8.5), 600 rpm of agitation, 1 liter of volume and temperature of 25˚C. during the precipitation tests, three parameters were then varied: pH (8; 8.5; 9; 9.5; and 10), time (1 and 2 hours); and temperature (25˚C and 50˚C). The experimental design applied to perform the different combinations of parameters is presented in Table 2. These tests were carried out on 1.5 liters samples with an agitation of 800 rpm.

Operating mode

The procedure used for the manganese carbonate precipitation tests is as follows:

- Take 1500 ml of the test sodium (overflow from the decanter) with the test tube;
- Place this volume in a 5000 ml beaker;
- Place in the beaker and start the mechanical stirrer at 800 rpm;

Table 2. Experimental design of precipitation reactions.

N˚	pH	Time [Time]	Temperature [˚C]	N˚	pH	Time [Time]	Temperature [˚C]
1	8	1	25˚C	11	9	1	50
2	8	2	25˚C	12	9	2	50
3	8	1	50˚C	13	9.5	1	25
4	8	2	50˚C	14	9.5	2	25
5	8.5	1	25˚C	15	9.5	1	50
6	8.5	2	25˚C	16	9.5	2	50
7	8.5	1	50˚C	17	10	1	25
8	8.5	2	50˚C	18	10	2	25
9	9	1	25	19	10	1	50
10	9	2	25	20	10	2	50

- Place the electrode of the pH meter in the solution;
- Using a burette, add the sodium carbonate solution previously prepared at 100 g/l until the pH of the test is reached;
- Once the pH set point is reached, start the timer;
- Adjust the pH by adding the sodium carbonate solution with a syringe;
- Stop the precipitation when the set time for the test is reached;
- Filter and wash the resulting precipitate;
- Dry the precipitate in the oven;
- Weight the dry precipitate using a precision balance;
- Take a volume of the filtrate to be analyzed;
- Prepare the precipitate for content analysis.

2) Calcination tests

Material and method

The equipment used during the calcination tests includes a precision electronic balance brand OHAUS, a furnace brand VECSTAR FURNACE, steel crucibles and other tools (spatula, cup, tweezers, markers, pen, chronometer, and envelope). The calcined samples come from a manganese carbonate precipitation carried out under the optimal conditions retained during the precipitation tests.

The temperature and time of calcination were the only two varied parameters at 370˚C, 420˚C then 470˚C and 1, 2, 3 then 4 hours, respectively.

Operating mode

The procedure applied during the calcination tests is as follows:

- Turn on the oven, set it to the temperature required for the test;
- Wait until the oven temperature set for the test;
- Weight 5 g of the precipitation obtained under the condition validate during the precipitation tests;
- Place the weighed 5 g in a crucible, place the crucible in the oven and start the timer;
- When the set time is reached, remove the crucible from the oven;
- Weight the calcined sample and store it in an envelope.

4. Results

Precipitation tests

Influence of parameters and interaction effects on precipitation yield.

The data contained in **Table 3** is used to represent the influence of the parameters on the precipitation yield using the graph presented in **Figure 2**.

Furthermore, it is also possible to observe the effects of different possible interactions on the precipitation yield (**Figures 3-5**).

The following findings and interpretations can be made from the analysis of **Figure 2**:

- The precipitation time does not have a significant impact on the precipitation yield because between 1 and 2 hours, there are only slight variations in three yields.

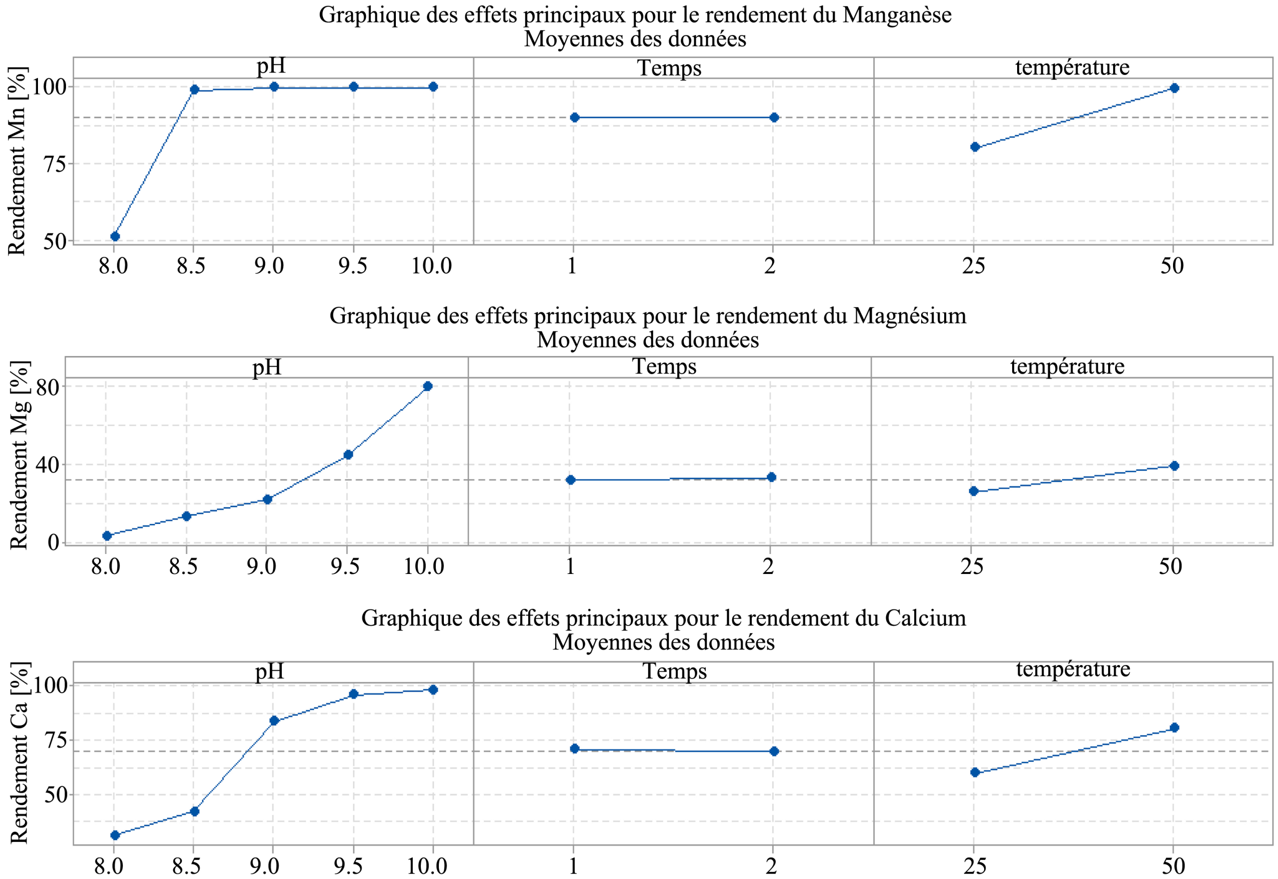


Figure 2. Influence of parameters on precipitation yields.

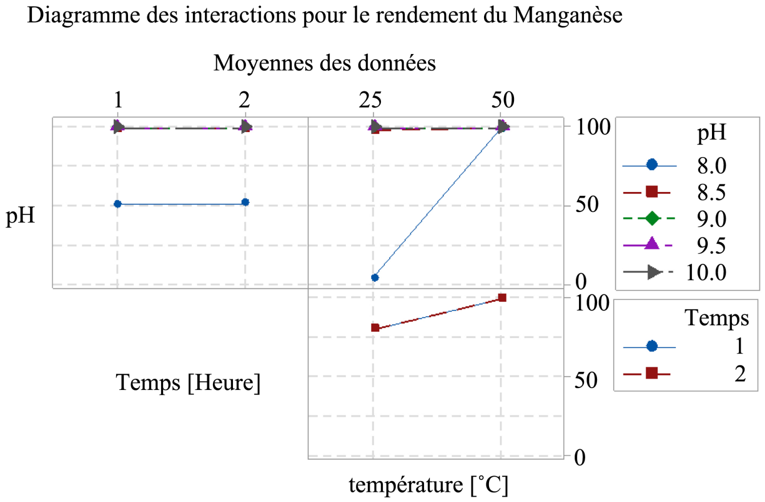


Figure 3. Effect of parameter interaction on manganese precipitation efficiency.

- The increase in temperature is manifested by an increase in the precipitation yield not only of manganese but also of magnesium and calcium. This observation can be explained by a more important diffusion, when the temperature increases, of the ions (in particular Mn^{2+}, Mg^{2+} and Ca^{2+}, which precipitate in contact with the CO_3^{2-}).

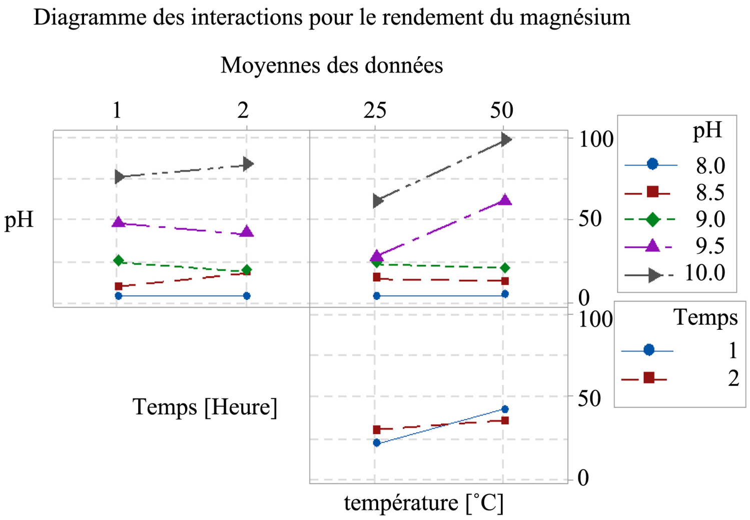


Figure 4. Effect of parameter interaction on magnesium precipitation efficiency.

Table 3. Precipitation yield and content of Mn, Mg, Ca in the precipitate.

N˚	Precipitation efficiency			Precipitate content		
	Mn [mg/l]	Mg [mg/l]	Ca [mg/l]	Mn [%]	Mg [%]	Ca [%]
1	3.00	1.186	3.843	-	-	-
2	4.43	4.390	7.256	-	-	-
3	99.04	4.669	63.151	21.41	3.111	5.642
4	99.28	2.229	48.380	21.56	3.036	4.616
5	98.43	9.736	10.501	24.21	1.126	3.302
6	98.18	18.249	15.140	24.05	1.018	3.568
7	99.87	7.888	62.160	20.26	4.373	5.835
8	99.93	16.100	79.424	19.01	4.970	5.648
9	99.83	19.329	85.123	19.54	4.860	6.133
10	99.94	26.487	90.385	17.83	5.584	5.856
11	99.99	29.365	94.771	16.06	8.168	5.509
12	99.95	10.910	62.899	19.18	5.897	4.663
13	99.99	22.608	94.593	15.40	6.965	4.980
14	99.99	31.841	96.061	15.67	7.781	4.909
15	99.99	72.429	95.412	10.40	14.001	3.258
16	99.99	50.123	96.869	11.78	11.240	3.883
17	99.99	53.957	95.524	14.92	8.540	4.985
18	99.99	68.280	97.012	13.45	9.031	4.552
19	99.99	98.102	98.823	8.27	15.606	2.802
20	99.99	98.838	99.679	7.78	14.802	2.609

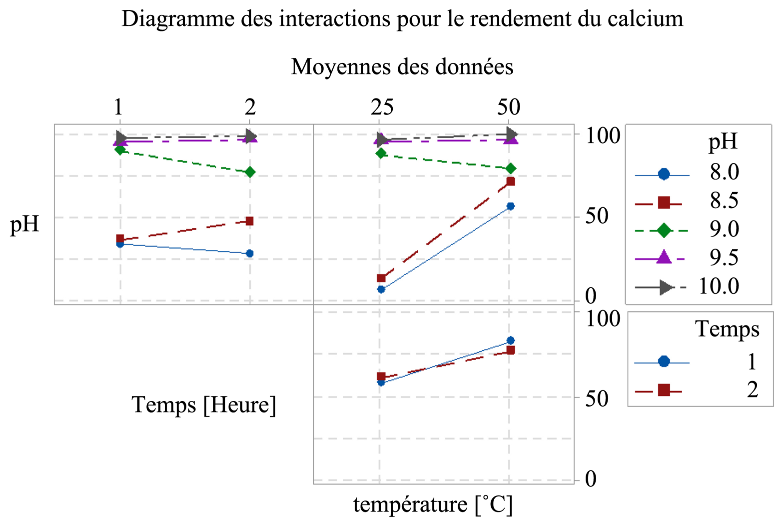


Figure 5. Effect of parameter interaction on Calcium precipitation efficiency.

- The manganese precipitation yield increases when the precipitation pH increases. However, it can be seen that from pH 8.5 onwards, this yield hardly changes at all. This phenomenon could be explained by the fact that the Mn^{2+} is the first to precipitate because of its affinity for the CO_3^{2-} (greater than that of the other ions in solution), almost all of the manganese is then eliminated from the solution very early on, so that its precipitation yield no longer changes.
- The calclium precipitation efficiency curve does not evolve significantly from a pH equal to 9. This point could correspond to the exhaustion almost of all the calcium present in solution.

According to the interactions, the graphs obtained are as follows:

These figures give the following conclusions:

- The pH-Time interaction: this interaction does not have a significant impact on the precipitation yield of manganese. On the other hand, we notice some variations in the precipitation yield of calcium and magnesium. Indeed, the yields of Ca and Mg increase between 1 and 2 hours for pH 8.5 and 10, but the yield decreases for pH 8, 9 and 9.5 when moving from 1 to 2 hours.
- The pH-Temperature interaction: when the temperature varies from 25˚C to 50˚C, this interaction leads to an increase in precipitation yield for pH values of 8 and 8.5 (for Mn and Ca) and pH values of 9.5 and 10 (for Mg).
- Time-Temperature interaction: this interaction does not have a remarkable impact on the precipitation yields. Indeed, we can see that the curves are almost parallel at 1 hour as well as at 2 hours.

Assumption of an optimum for the precipitation yield

The objective is to maximize the precipitation of manganese while minimizing the co-precipitation of magnesium and calcium.

From the analysis and interpretation of the main effects graph, it can be assumed that the optimum is at 1 hour, 25˚C and pH 8.5. This assumption is based on the following facts:

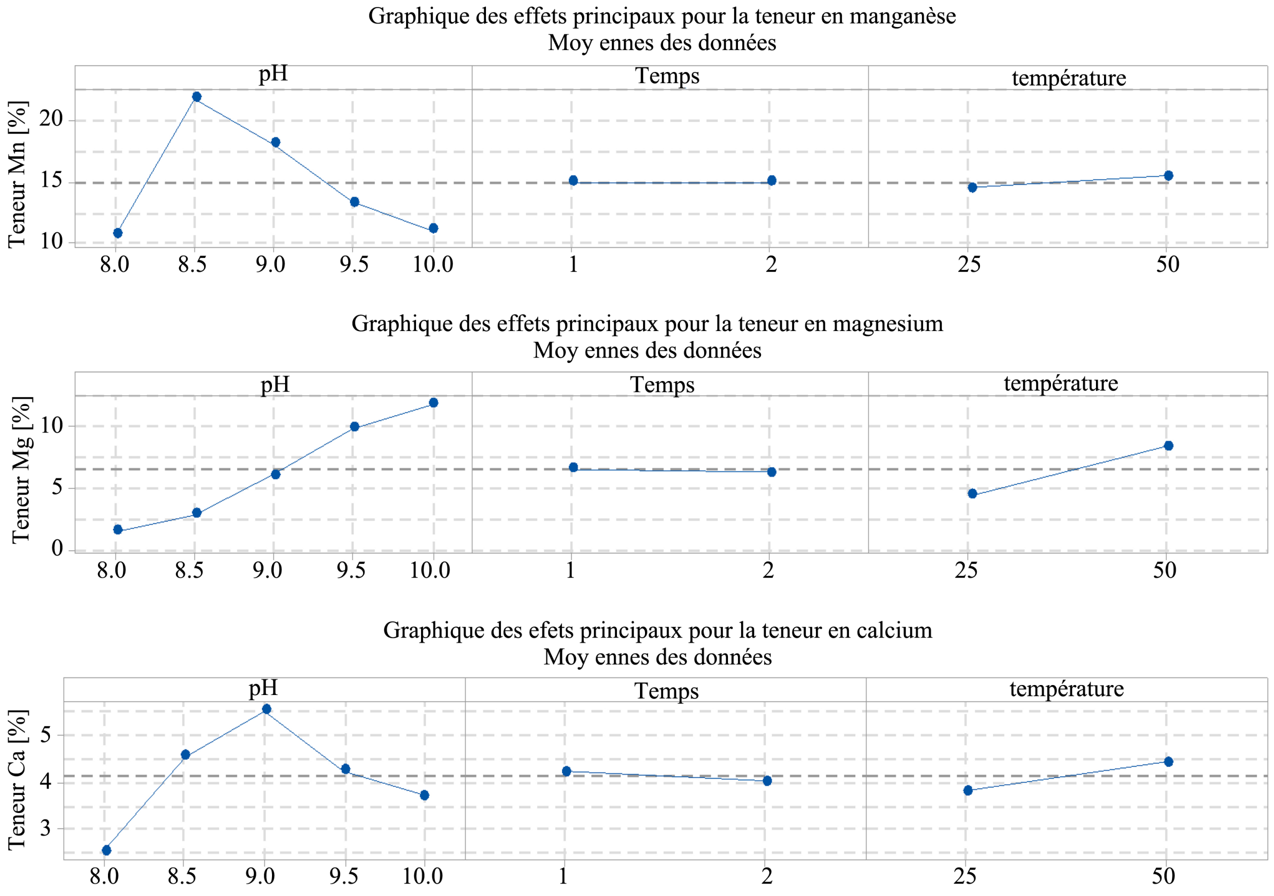
- It can be seen that time does not significantly influence the precipitation yields in the chosen range, so there is no point in extending the precipitation to 2 hours when the amount of manganese that can be precipitated has been reached in one hour ;
- Although the increase in temperature increases the yield of manganese precipitation, it is preferable to work at room temperature, because, it is necessary to minimize the co-precipitation of Mg and Ca which would also be favored by the increase in temperature;
- From a pH of 8.5 onwards, the manganese precipitation yield changes only slightly. Going beyond this pH would only serve to precipitate more impurities.

Influence of parameters and interaction effects on the quality of the precipitate

As for the precipitation yield, it is possible to represent the influence of the parameters on the quality of the precipitate (**Figure 6**) as well as the effects of the different interactions (**Figures 7-9**) based on the data contained in **Table 3**.

The following findings and interpretations are then made:

- The precipitation time does not influence the quality of the precipitate obtained;



Graphique des effets principaux pour la teneur en manganèse
Moy ennes des données

Graphique des effets principaux pour la teneur en magnesium
Moy ennes des données

Graphique des efets principaux pour la teneur en calcium
Moy ennes des données

Figure 6. Influence of the parameters on the quality of the precipitate.

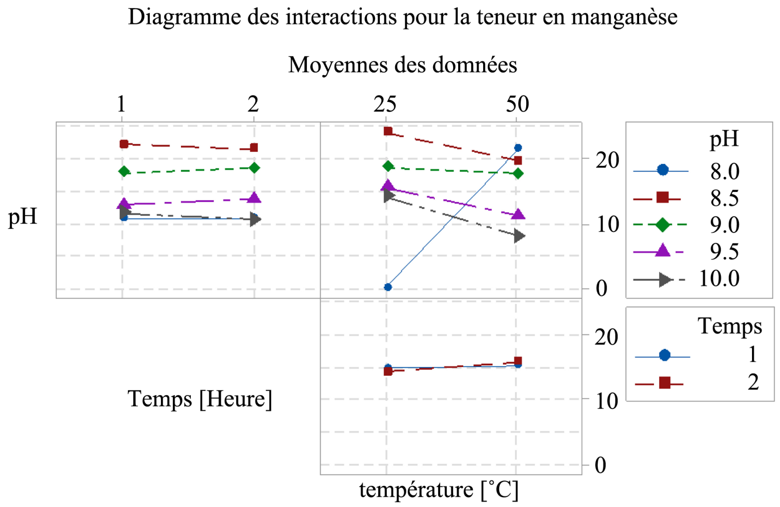


Figure 7. Effect of interaction between parameters on manganese content.

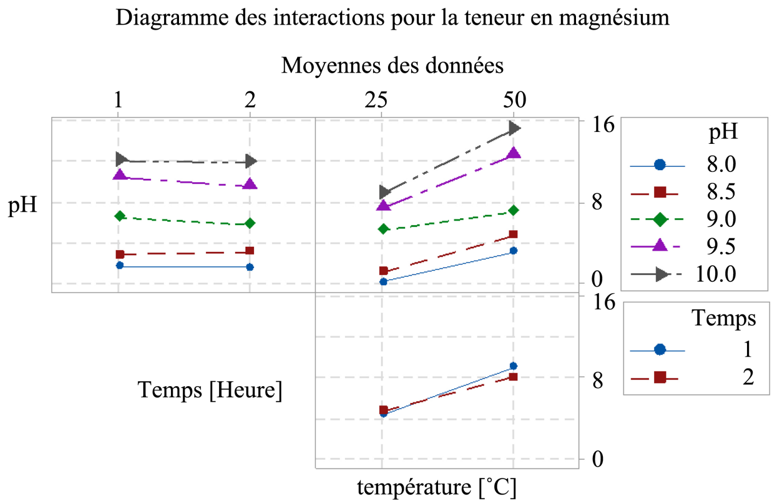


Figure 8. Effect of interaction between parameters on magnesium content.

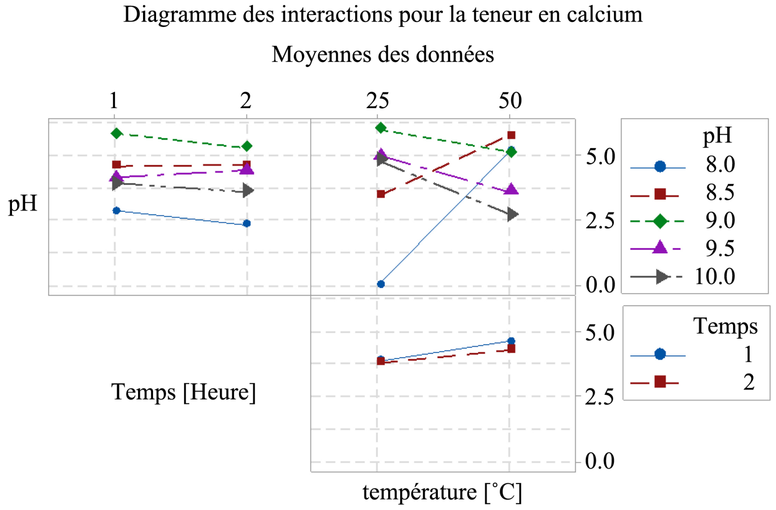


Figure 9. Effect of interaction between parameters on Calcium content.

- The increase in temperature only slightly increases the content of manganese in the precipitate; on the other hand, it can be seen that the increase in the content of impurities (Mg and Ca) is favored by an increase in temperature. The consequence is that it would not be judicious to work so as not to favor this phenomenon.
- The maximum manganese and calcium contents in the precipitate are obtained for pH 8.5 and 9 respectively. These points would correspond to the depletion of manganese and calcium in the solution.
- The curve of the magnesium content in the precipitate does not have a maximum. This could be explained by the fact that above pH 10, the precipitation of magnesium should continue and thus increase its content in the precipitate.

We noticed the interactions in **Figures 7-9**.

The analysis of these interactions leads to the following assessment:

- The pH-Time interaction: for all pH values, the passage from 1 hour to 2 hours produces only very small variations in the content of Manganese, Magnesium and Calcium in the precipitate.
- The pH-Temperature interaction: the passage from 25˚C to 50˚C results in a decrease in the manganese content for all pH values except pH 8. In the case of magnesium, there is an increase in the content in the precipitate for all pH values. As for calcium, there is a decrease in the content in the precipitate (except in the case of pH 8 and 8.5).
- The Time-Temperature interaction: the lines are almost parallel, which indicates that this interaction has no major effect on the contents of Mn, Mg and Ca in the precipitate.

Assumption of an optimum for the quality of the precipitate

From the analysis of the main effects diagrams of the factors on the contents, the following optimal conditions emerge:

- ➢ 1 hour: because the content of the element in the precipitate is not significantly influenced by the precipitation time;
- ➢ 25˚C: because an increase in temperature results in a considerable increase in the content of impurities;
- ➢ pH 8.5: this pH corresponds to the highest manganese content obtained in the precipitate.

These considerations add to those found in the precipitation yield.

Conclusion on the optimum precipitation of manganese carbonate

Based on the interpretations of results made for precipitation yields and precipitate quality, the final optimal conditions selected will therefore be:

- pH = 8.5;
- Time = 1 hour;
- Temperature: 25˚C.

Calcination tests

The calculated mass losses during calcination tests are presented in **Table 4**.

Table 4. Loss of mass obtained during calcination tests.

N°	Temperature	Time	Δm [%]	N°	Temperature	Time	Δm [%]
1	370˚C	1 hour	21.00	7	420˚C	3 hours	28.00
2	370˚C	2 hours	26.60	8	420˚C	4 hours	33.50
3	370˚C	3 hours	22.50	9	470˚C	1 hour	34.40
4	370˚C	4 hours	25.50	10	470˚C	2 hours	37.80
5	420˚C	1 hour	31.80	11	470˚C	3 hours	38.00
6	420˚C	2 hours	33.43	12	470˚C	4 hours	43.50

Based on the data in Table 4, the influence of the parameters and their interactions with respect to the mass loss were evaluated as shown in Figure 10 and Figure 11.

Based on the above graphs, we found the following assessments:

- As expected, the increase in calcination temperature results in an increase in mass loss *i.e.* an increase in CO_2 released during the reaction (Figure 10). This phenomenon could be explained by the fact that the increase in temperature results in an increase in the affinity of carbonate decomposition as predicted by the thermodynamic data in Table 1;
- When the calcination time increases (Figure 10): the loss of mass increases as one would expect; indeed, this phenomenon would translate the prolongation of the reaction in time allowing a greater quantity of carbonate to decompose. However, a decrease in mass loss is observed at three hours of calcination and this is for all calcination temperatures (as shown in Figure 11).
- The similar shapes of the mass loss curves at different temperatures (Figure 11) indicate that the time-temperature interaction during calcination has no significant effect on mass loss.

Results and Discussion

The interpretations made on the above results can be summarized as follows: the two orientation tests confirm the alleged theoretical considerations, which predict better precipitation of manganese by means of carbonate and an inevitable co-precipitation of calcium and magnesium present in solution. In the same vein, the results of the precipitation tests illustrate the high precipitation affinity of manganese carbonate with high values of precipitation yield (as predicted by the concepts presented in Section 2.1).

The following elements should be noted: analysis of the precipitation yields and the quality of the precipitates indicates that the optimum for manganese carbonate precipitation is obtained at 25˚C, 1 hour and a pH of 8.5 (conditions for carrying out test 5); which corresponds to a precipitation yield and a manganese content in the precipitate around 98.43% and 24.41% respectively. The co-precipitation is 9.736% for Magnesium and 10.501% for calcium. This gives an impurity content in the precipitate equal to 1.126% magnesium and 3.302% calcium.

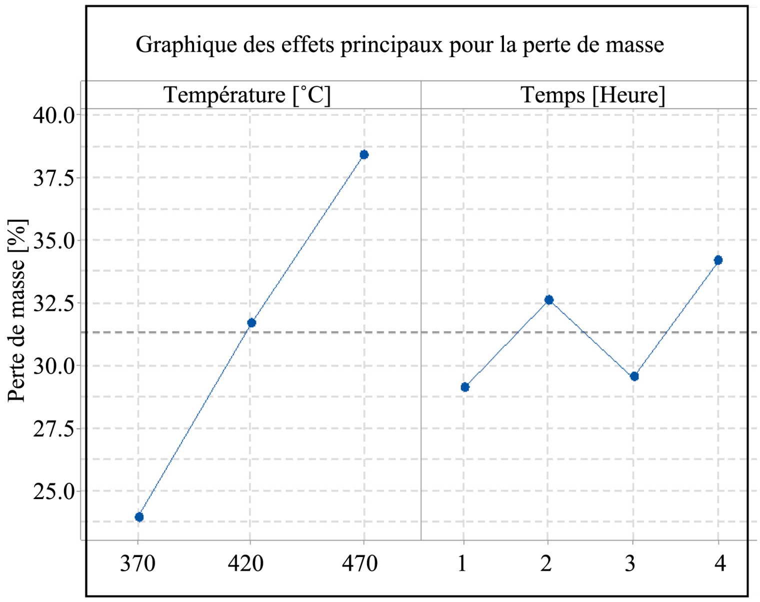


Figure 10. Influence of parameters on mass loss.

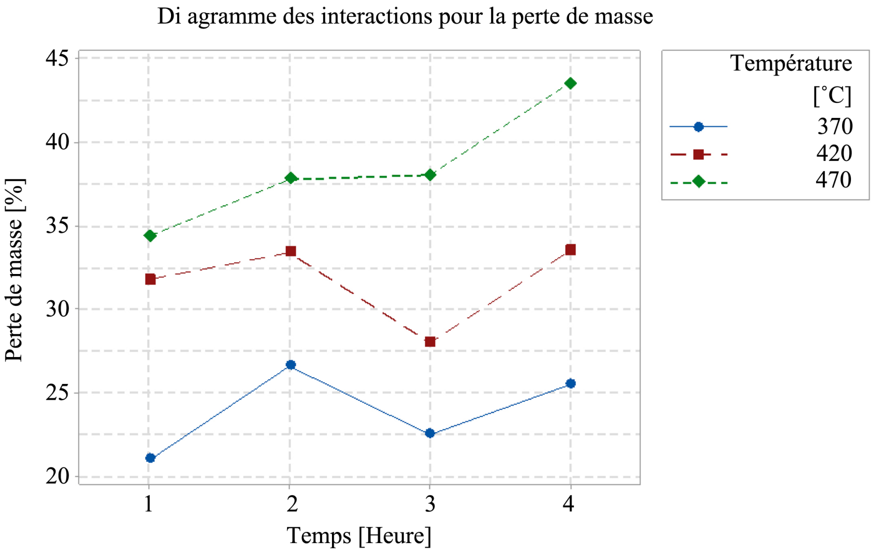


Figure 11. Effect of parameter interaction on mass loss.

As for the calcination tests, the values of the mass losses obtained (ranging from 20 to more than 40%) reassure us that the prediction of the temperature range during calcination (made in Section 2.2) was adequate; although, in the absence of a means of evaluating the relative contents of the oxides formed, it appears difficult to explain the causes of the drop in mass loss observed at three hours of calcination.

5. Conclusions

Manganese recovery was done in the form of manganese carbonate by means of sodium carbonate. The results obtained show an efficient recovery of manganese at 25˚C, at one hour and at a pH of 8.5 with a precipitation yield and a manganese content in the precipitate around 98.43% and 24.21% respectively, co-precipitation is 9.736% for magnesium and 10.501% for calcium. This gives an impurity content in the precipitate equal to 1.126% magnesium and 3.302% calcium. During the calcination tests, it is observed, for a constant calcination time, an increase in the mass loss when the temperature increases.

Furthermore, increasing the calcination time at a given temperature causes an increase in mass loss. However, a significant decrease in mass loss is noted at three hours of calcinations and the greatest loss of mass at a temperature of 470˚C after four hours of calcination. More studies have to bring light on oxide evaluation proportions contained in the calcinate materials.

Performing a manganese carbonate precipitation after acid leaching of a manganese ore would be a sensible way to not only study the precipitation of manganese from a sulfate solution with a high manganese concentration, but also to obtain larger amounts of the precipitate. In addition, an x-ray diffraction analysis would allow the determination of the proportions of oxides obtained during calcination. The method chosen here was to precipitate manganese in the form of a high-quality carbonate and then to calcine the carbonate obtained under conditions that would favor the obtaining of manganese dioxide. An experience plan (Taguchi method) was applied in order to simplify the experimental protocol and show out the factor's effect on the response, which can easily be a variable in a process or even a measure of the quality of the product.

Acknowledgements

We would like to thank the Ruashi Mining laboratory for allowing the sampling and precipitation tests to be carried out in their facilities. We also thank the managers of the Physical Chemistry Laboratory at the Polytechnic Faculty/University of Lubumbashi and the staff of that laboratory for their availability.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Wang, S.Y. and Fan, X.Y. (2019) Flexible Zinc-Manganese Dioxide Alkaline Batteries based on Kelp Electrolytes. *Journal of Science and Chemical Engineering*, **7**, 19-28. https://doi.org/10.4236/msce.2019.712003

[2] He, Y., Matthews, B., Wang, J., Song, L., Wang, X.X and Wu, G. (2018) Innovation and Challenges in Materials Design for Flexible Rechargeable Batteries: From 1D to 3D. *Journal of Materials Chemistry A*, **6**, 735-753. https://doi.org/10.1039/C7TA09301B

[3] Wang, X.F., Lu, X.H., Liu, B., Chen, D., Tong, Y.X. and Shen, G.Z. (2014) Flexible Energy-Storage Devices: Design Consideration and Recent Progress. *Advanced Materials*, **26**, 4763-4782. https://doi.org/10.1002/adma.201400910

[4] Liu, H.-G. and Zhu, G.-C. (2007) Removal of Ca (II), Mg (II) from Leaching Solution of Low Grade Manganese Ore by Precipitation with Fluoride. *Mining & Metallurgy*, **16**, 25-28. (In Chinese)

[5] Yan, S. and Qiu, Y.-R. (2014) Preparation of Electronic Grade Manganese Sulfate from Leaching Solution of Ferromanganese Slag. *Transactions of Nonferrous Metals Society of China*, **24**, 3716-3721. https://doi.org/10.1016/S1003-6326(14)63520-2

[6] P. Muzadi, and Kotze, M. (2013) A New Development in the Oxidative Precipitation of Fe and Mn by SO_2/Air. *The Journal of the Southern African Institute of Mining and Metallurgy*, 223-234.

[7] Lin, Q., Fu, J., Gu, G., Wang, C., Wang, H., Zhu, R. and Liu, Y. (2016) Separation of Manganese from Calcium and Mangnesium Sulfate Solutions via Carbonate Precipitation. *Nonferrous Metals Society of China*, **26**, 1118-1125. https://doi.org/10.1016/S1003-6326(16)64210-3

[8] Zhang, W., Cheng, C.Y., and Pronolo, Y. (2010) Investigation of Methods for Removal and Recovery of Manganese in Hydrometallurgical Process. *Hydrometallurgy*, **101**, 58-63. https://doi.org/10.1016/j.hydromet.2009.11.018

[9] Shu, J., Wu, H., Chen, M., Peng, H., Li, B., Liu, R., Liu, Z., Wang, B., Huang T. and Hu, Z. (2019) Fractional Removal of Manganese and Ammonia Nitrogen from Electrolytic Metal Manganese Residue Leachate Using Carbonate and Struvite Precipitation. *Water Research*, **153**, 229-238. https://doi.org/10.1016/j.watres.2018.12.044

[10] Kamgaing, T. (2015) Precipitation of Divalent Cation Carbonates in Lake Systems: Interest, State of Knowledge of Mechanismes and Suggestions. *Water Science Journal*, **28**, 81-102.