Communication

Thermodynamic Simulations for Determining the Recycling Path of a Spent Lead-Acid Battery Electrolyte Sample with Ca(OH)\textsubscript{2}

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Featured Application: This thermodynamic simulation can help design the recycling process of spent lead-acid battery electrolyte. The effect of ambient CO\textsubscript{2} and pH can be simulated by thermodynamic calculations.

Abstract: By utilizing thermodynamic calculations, the possible removal path of spent lead-acid battery electrolytes was modeled. The process was divided into precipitation and carbonation processes. In the carbonation process, two scenarios were discussed, namely carbonation with and without pre-filtration of the precipitates resulted from the precipitation process. The results showed that in the precipitation process, the theoretical limit for the chemical removal of SO\textsubscript{4}^{2−} was 99.15%, while in the following carbonation process without filtration, only 69.61% of SO\textsubscript{4}^{2−} was removed due to the fact that CO\textsubscript{2} reacts with Ca\textsuperscript{2+} ion in the solution, and thus leads to the production of CaCO\textsubscript{3} and SO\textsubscript{4}^{2−} ions in the solution. In the carbonation process without filtration, with the increase of CO\textsubscript{2} in the solution the removal ratio of SO\textsubscript{4}^{2−} further decreases. Thermodynamic simulation was effective in predicting the theoretical removal limits and helps in understanding and optimizing the removal process.

Keywords: thermodynamic simulations; spent lead-acid battery; electrolyte; carbonation

1. Introduction

Lead-acid batteries (LAB) are widely used in motor vehicles \cite{1,2}, backup power supplies \cite{3}, and stand-alone power systems \cite{4,5} due to their properties of excellent reliability, low cost, good operation life, high surge currents, and relatively large power-to-weight ratio \cite{6}. LABs, as the single most-used battery system worldwide, consume approximately 85% of the total global lead production \cite{7}. To satisfy the huge and ever-increasing demand for lead worldwide, in 2014 alone 2.46 million tons of secondary lead was recovered from spent LABs. \cite{8} The first step in the recycling process is disassembly, in which spent LABs are separated into four parts, i.e., the grid, with the main composition being lead (92~95%), lead paste, which is mainly composed of lead oxide (PbO), lead dioxide (PbO\textsubscript{2}), lead sulfate (PbSO\textsubscript{4}), and lead (Pb) plastics, which are the main composition of shells, and electrolytes, with the main composition being sulfate acid (38 wt.% H\textsubscript{2}SO\textsubscript{4}). The grid separated from spent LABs is commonly refined for utilization in the manufacture of new LABs \cite{9}. The lead paste has been intensively studied with various hydrometallurgy and pyrometallurgy
techniques [10–14]; shells are also recovered as polypropylene for manufacturing new LABs [15,16], and the electrolytes are normally collected for further purification [8]. However, in spent LAB recycling plants, installation of new devices is required to collect and handle the highly corrosive electrolytes. In a typical disassembly and refinery plant, spent electrolytes are often discharged onto the ground and collect in a pit, which makes the purification process unreasonable for recycling. The typical recycling methods of SO$_4^{2-}$ ions from wastewater include: adsorption [17], chemical precipitation [18,19], biological treatment [20], and ion exchange [21]. Due to the high concentrations of SO$_4^{2-}$ in the spent electrolytes, chemical precipitation was adopted. BaCl$_2$ [22], limestone [19], and ettringite [23] have been used to remove SO$_4^{2-}$ in wastewater, while no detailed theoretical calculation has been reported. In this paper, the systematic theoretical calculations of spent LAB electrolytes’ reactions with Ca(OH)$_2$ were conducted, and sulfate ions were then recovered as CaSO$_4$·2H$_2$O. Thermodynamic calculations were utilized to simulate the whole process, based on which the optimum conditions and recycling path were obtained. The thermodynamic simulation predicted the theoretical chemical precipitation removal efficiency and suggested that ambient CO$_2$ should be avoided in the precipitation process and filtration should be adopted before the carbonation process to achieve higher efficiency.

2. Materials and Methods

2.1. Materials

The spent LAB electrolyte sample was received from Dansuk Industrial Co., Ltd., Gyeonggi-do, Korea. The spent electrolyte sample was first filtered and analyzed with Inductively coupled plasma-optical emission spectrometry (ICP-OES) to measure the concentration of SO$_4^{2-}$ ions. The concentration of SO$_4^{2-}$ in the spent electrolyte was 147,000 mg/L. The main impurities of the spent electrolyte were Ca$^{2+}$, Mg$^{2+}$, and Pb$^{2+}$ (3.01 mg/L). Due to the low concentrations of both Ca$^{2+}$ and Mg$^{2+}$ and the fact that both ions are not toxic, only Pb$^{2+}$ was discussed in detail in this research. The pH of the spent electrolyte solution was measured with a Thermo Scientific® Orion® Versa Star Pro™ pH meter equipped with a highly sensitive ROSS Ultra 8302BNUMD electrode, with the mean pH being −0.53.

2.2. Methods

The thermodynamic calculations were carried out with Matlab® R2010a software using thermodynamic parameters of all possible reactions. At the first stage, spent H$_2$SO$_4$ from the electrolyte sample was precipitated with Ca(OH)$_2$ powder until the solution was almost saturated calcium hydroxide, then the carbonation processes were simulated, both with and without pre-filtration of the precipitates resulted from the precipitation process. All simulations were performed under the condition that the temperature was kept at 25 °C at all times. Equations (1)–(3), (4)–(13), and (14)–(21) from Table 1 were used in the calculation of the thermodynamic equilibrium distributions of the saturated solutions of Ca(OH)$_2$, CaCO$_3$, and CaSO$_4$·2H$_2$O, respectively, while Equations (21)–(29) and (30)–(43) from Table 1 were used to calculate the thermodynamic distributions of different species during the precipitation process and carbonation process after filtration of the precipitates. Equations (44)–(47), together with Equations (23), (24), (26)–(29), (34), (35), (37), and (39) from Table 1, were utilized to calculate the carbonation process without the filtration of precipitates resulted from the precipitation process. Equations (48)–(55) and (56)–(61) from Table 1 were used to calculate the thermodynamic distributions of Pb$^{2+}$ in precipitation and carbonation processes, respectively. All species (aqueous species and precipitates) at different pH can be obtained by solving the matrix of equilibrium constants and mass balances.

It is worth pointing out that in the modeling process of carbonation, the system was considered as a closed system with a certain amount of CO$_2$ injected into the system. This was adopted due to the fact that CO$_2$ was the gas and the amount of CO$_2$ consumed cannot be easily obtained.
Due to the fact that calcium, sulfate, and carbonate are all divalent ions with quite low ionic activity coefficients (\(\gamma\)), which are \(\gamma_{Ca^{2+}} = 0.28\) (\(I = 0.7, 25^\circ C\) and 1 atm), \(\gamma_{SO_4^{2-}} = 0.12\), and \(\gamma_{CO_3^{2-}} = 0.20\) (\(I = 0.7, 25^\circ C\) and 1 atm), respectively, the activity corrections are needed in the thermodynamic modeling process. The definition of ionic strength \(I\) and activity coefficient are shown in Equations (1) and (2) [24]:

\[
I = 1/2 \sum m_i Z_i^2
\]

\[
\gamma_i = \frac{a_i}{m_i}
\]

where \(m_i\) is the molality of an aqueous species, \(i\) is the corresponding aqueous species, \(Z_i\) is the charge of \(i\), \(a_i\) is activity of species \(i\), and \(\gamma_i\) is the activity coefficient of species \(i\). In this study, a simplified Helgeson-Kirkham-Flowers model was used to calculate the activity coefficient, as shown in Equation (3) [25–27]:

\[
\log \gamma_i = -AZ_i^2 \left( \sqrt{\frac{I}{1 + bI}} \right) - \log(1 + 0.018 \sum m_k) + bI
\]

where \(A\) is the Debye-Hückel slope, \(B\) is the distance of the closest approach, \(b\) is a solute specific parameter, and \(k\) is all solute species in the aqueous solution.

3. Results

3.1. Precipitation

Figure 1 shows the thermodynamic calculations of 30 mM Ca(OH)\(_2\) in aqueous solution at 25 °C with different pH. The theoretical values were obtained by solving the matrix consisting of both equilibrium constants (Equations (2) and (3) from Table 1) and mass balances (Equations (4) and (5)). With Matlab, this set of equations were simultaneously solved with 100 steps in the whole pH range (0–14), thus giving the distribution of each species at different pH. In the case of Ca(OH)\(_2\) solution, four species, Ca\(^{2+}\), CaOH\(^+\), OH\(^-\), and Ca(OH)\(_2\)(s), were taken into consideration. Figure 1a shows the log concentrations of different species in 30 mM Ca(OH)\(_2\) solution with different pH. Log concentrations were adopted due to the low concentrations of each species. As can be seen, with the increase of pH the concentration of Ca\(^{2+}\) first stays unchanged when pH < 12.6, while with the further increase of pH, the concentration of Ca\(^{2+}\) decreased slowly, and at the same time Ca(OH)\(_2\)(s) emerged in the solution as a precipitate. CaOH\(^+\) ions started to appear at pH 6, the log concentration of which increased linearly until pH 12.6, after which the log concentration of CaOH\(^+\) ions started to decrease linearly. In Figure 1b, the fraction of calcium was calculated vs. pH, and a similar change of concentration was also observed for Ca\(^{2+}\), CaOH\(^-\), and Ca(OH)\(_2\). The theoretical parameters of saturated Ca(OH)\(_2\) are shown in Table 1; as can be seen, the theoretical pH of saturated Ca(OH)\(_2\) is 12.45 with C\(_{Ca^{2+}}\) = 19.48 mM. Similarly, the equilibrium distributions of saturated CaCO\(_3\) solution can be calculated by solving the matrix composed of Equations (4)–(13) from Table 1 (thermodynamic parameters) and (6)–(8) (mass balances). The distributions of different species in CaCO\(_3\) solution was also shown in Figure 2 and Table 1. As can be seen, for the saturated solution of CaCO\(_3\), the equilibrium pH is 9.94 and C\(_{Ca^{2+}}\) = 0.1415 mM. For the saturated CaCO\(_3\) solution, if the pH is high enough (pH > 13), Ca\(^{2+}\) from CaCO\(_3\) will dissolve into solution and form Ca(OH)\(_2\)(s), thus causing the increase of concentration of free Ca\(^{2+}\) ions. As for saturated CaSO\(_4\) solution (Figure 3), the equilibrium pH is 7.08 and the equilibrium C\(_{Ca^{2+}}\) = 12.03 mM. In the saturated solution of CaSO\(_4\), the main precipitate would be CaSO\(_4\)·2H\(_2\)O; as can be seen from Figure 3b, with the increase of pH CaSO\(_4\)·2H\(_2\)O starts to decrease at pH 11 and the dominant precipitate becomes Ca(OH)\(_2\)(s) at approximately pH 13. Therefore, for recovering CaSO\(_4\)·2H\(_2\)O, the pH should be controlled properly. By comparing the data in Figures 1 and 2, it is clear that the equilibrium concentration of Ca\(^{2+}\) in CaCO\(_3\) solution was significantly smaller than that in Ca(OH)\(_2\) solution, which was caused by the much smaller solubility products (K\(_{sp}\)) of CaCO\(_3\), and should carbonation
happen in the precipitation process the concentration of Ca$^{2+}$ should also decrease, which would, in turn, cause the increase of SO$_4^{2-}$. Based on the results obtained from Figures 1–3, we conclude that the saturated CaCO$_3$ solution has the lowest equilibrium $C_{Ca^{2+}}$, and contacting with CO$_2$ might decrease the concentration of Ca$^{2+}$ ions, which will help us better understand the carbonation process discussed in Section 3.2. The detailed species distribution of saturated Ca(OH)$_2$, CaCO$_3$ and CaSO$_4$ can be found in Table 2.

Table 1. Chemicals, formulas, reactions, and equilibrium constants used in the thermodynamic calculations.

| Formulas | Possible Chemical Reactions | Log$_{10}(K)$ $^1$ |
|----------|-----------------------------|---------------------|
| H$^+$/OH$^-$ | H$_2$O ↔ H$^+$ + OH$^-$ | (1) −13.99 |
| Ca$^{2+}$ | 2H$^+$ + Ca(OH)$_2$(s) ↔ Ca$^{2+}$ + 2H$_2$O | (2) 22.62 |
| CaOH$^+$ | H$^+$ + Ca(OH)$_2$(s) ↔ CaOH$^+$ + H$_2$O | (3) 9.785 |
| Ca(OH)$_2$(s) | CaCO$_3$(s) + 2H$_2$O ↔ 2H$^+$ + 2CO$_3^{2-}$ + Ca(OH)$_2$(s) | (4) −30.88 |
| Ca(OH)$_2$(s) | CaCO$_3$(s) + H$_2$O ↔ 2H$^+$ + 2CO$_3^{2-}$ + Ca(OH)$_2$(s) | (5) −41.0 |
| CaCO$_3$ | CaCO$_3$(s) ↔ CaCO$_3$ | (6) −4.961 |
| CaCO$_3$ | CaCO$_3$(s) ↔ CaCO$_3$ | (7) 3.08 |
| CaOH$^+$ | CaCO$_3$(s) + H$_2$O ↔ H$^+$ + 2CO$_3^{2-}$ + CaOH$^+$ | (8) −21.11 |
| CO$_2$ | 2H$^+$ + CO$_3^{2-}$ ↔ H$_2$O + CO$_2$ | (9) 16.68 |
| CO$_2$(g) | 2H$^+$ + CO$_3^{2-}$ + H$_2$O ↔ CO$_2$(g) | (10) 18.15 |
| H$_2$CO$_3$ | 2H$^+$ + CO$_3^{2-}$ ↔ H$_2$CO$_3$ | (11) 16.70 |
| HCO$_3^−$ | H$^+$ + CO$_3^{2-}$ ↔ HCO$_3^−$ | (12) 10.33 |
| Ca$^{2+}$ | CaCO$_3$(s) ↔ Ca$^{2+}$ + CO$_3^{2−}$ | (13) −8.30 |
| CaOH$^+$ | CaSO$_4$(s) + H$_2$O ↔ CaOH$^+$ + H$^+$ + SO$_4^{2−}$ | (14) −17.21 |
| CaSO$_4$ | CaSO$_4$(s) ↔ CaSO$_4$ | (15) −2.190 |
| Ca$^{2+}$/SO$_4^{2−}$ | CaSO$_4$(s) ↔ Ca$^{2+}$ + SO$_4^{2−}$ | (16) −4.378 |
| Ca(OH)$_2$(s) | CaSO$_4$(s) + 2H$_2$O ↔ Ca(OH)$_2$(s) + 2H$^+$ + 2SO$_4^{2−}$ | (17) −26.99 |
| Ca(OH)$_2$(s) | CaSO$_4$(s) + H$_2$O ↔ Ca(OH)$_2$(s) + 2H$^+$ + SO$_4^{2−}$ | (18) −37.08 |
| CaSO$_4$2H$_2$O (s) | CaSO$_4$(s) + 2H$_2$O ↔ CaSO$_4$2H$_2$O(s) | (19) 0.161 |
| H$_2$SO$_4$ | 2H$^+$ + SO$_4^{2−}$ ↔ H$_2$SO$_4$ | (20) 0.780 |
| HSO$_4^{−}$ | H$^+$ + SO$_4^{2−}$ ↔ HSO$_4^{−}$ | (21) 1.982 |
| CaOH$^+$ | Ca(OH)$_2$(s) + H$^+$ ↔ H$_2$O + CaOH$^+$ | (22) 9.785 |
| CaSO$_4$ | CaSO$_4$2H$_2$O(s) ↔ CaSO$_4$(s) + 2H$_2$O | (23) −2.351 |
| Ca$^{2+}$ | Ca(OH)$_2$(s) + 2H$^+$ ↔ Ca$^{2+}$ + 2H$_2$O | (24) 22.62 |
| Ca(OH)$_2$(s) | Ca(OH)$_2$(s) ↔ Ca(OH)$_2$(s) + H$_2$O | (25) −10.09 |
| CaSO$_3$(s) | CaSO$_3$(s) + 2H$_2$O ↔ CaSO$_3$(s) + 2H$_2$O | (26) −0.161 |
| H$_2$SO$_4$ | CaSO$_4$2H$_2$O(s) ↔ CaSO$_4$(s) + 2H$_2$O | (27) −26.37 |
| HSO$_4^{−}$ | CaSO$_4$2H$_2$O(s) ↔ HSO$_4^{−}$ + Ca(OH)$_2$(s) + H$^+$ | (28) −25.17 |
| SO$_4^{2−}$ | CaSO$_4$2H$_2$O(s) ↔ SO$_4^{2−}$ + Ca(OH)$_2$(s) + 2H$^+$ | (29) −13.99 |
| CaCO$_3$ | Ca$^{2+}$ + CO$_2$ + H$_2$O ↔ CaCO$_3$ + 2H$^+$ | (30) 22.62 |
| CaHCO$_3^+$ | Ca$^{2+}$ + CO$_2$ + H$_2$O ↔ CaHCO$_3^+$ + H$^+$ | (31) 9.785 |
| CaOH$^+$ | Ca$^{2+}$ + H$_2$O ↔ CaOH$^+$ + H$^+$ | (32) −30.88 |
| CaSO$_4$ | Ca$^{2+}$ + SO$_4^{2−}$ ↔ CaSO$_4$ | (33) −41.0 |
| CO$_2$(g) | CO$_2$ ↔ CO$_2$(g) | (34) −4.961 |
| H$_2$CO$_3$ | CO$_2$ + H$_2$O ↔ H$_2$CO$_3$ | (35) 3.080 |
| H$_2$SO$_4$ | 2H$^+$ + SO$_4^{2−}$ ↔ H$_2$SO$_4$ | (36) −21.11 |
| HCO$_3^−$ | CO$_2$ + H$_2$O ↔ H$^+$ + HCO$_3^−$ | (37) 16.68 |
| HSO$_4^{−}$ | H$^+$ + SO$_4^{2−}$ ↔ HSO$_4^{−}$ | (38) 18.15 |
| CO$_2$(g) | CO$_2$ + H$_2$O ↔ 2H$^+$ + CO$_2$(g) | (39) 16.7 |
| Ca(OH)$_2$(s) | Ca$^{2+}$ + 2H$_2$O ↔ Ca(OH)$_2$(s) + 2H$^+$ | (40) 10.33 |
| CaCO$_3$(s) | Ca$^{2+}$ + 2H$_2$O + CO$_2$ ↔ CaCO$_3$(s) + H$_2$O | (41) −8.30 |
| CaSO$_3$(s) | Ca$^{2+}$ + SO$_3^{2−}$ ↔ CaSO$_3$(s) | (42) −17.21 |
| CaSO$_4$2H$_2$O(s) | Ca$^{2+}$ + SO$_4^{2−}$ + 2H$_2$O ↔ CaSO$_4$2H$_2$O(s) | (43) −2.19 |
| CaCO$_3$ | Ca(OH)$_2$(s) + CO$_2$ ↔ CaCO$_3$ + H$_2$O | (44) −4.378 |
| CaHCO$_3^+$ | Ca(OH)$_2$(s) + CO$_2$ + H$^+$ ↔ CaHCO$_3^+$ + H$_2$O | (45) −26.99 |
| CaOH$^+$ | Ca(OH)$_2$(s) + H$^+$ ↔ CaOH$^+$ + H$_2$O | (46) −37.08 |
| CaCO$_3$(s) | Ca(OH)$_2$(s) + CO$_2$ ↔ CaCO$_3$(s) + H$_2$O | (47) 0.161 |
| Pb(OH)$_2$ | Pb$^{2+}$ + 2H$_2$O ↔ Pb(OH)$_2$ + 2H$^+$ | (48) −17.12 |
| Pb(OH)$_3^−$ | Pb$^{2+}$ + 3H$_2$O ↔ Pb(OH)$_3^−$ + 3H$^+$ | (49) −28.06 |
Table 1. Cont.

| Species                  | Reaction                                                                 | \( K \) Value |
|--------------------------|--------------------------------------------------------------------------|----------------|
| \( \text{Pb}_2\text{(OH)}_4^{2+} \) | \( 2\text{Pb}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Pb}_2\text{(OH)}_4^{2+} + 4 \text{H}^+ \) | (50) -23.88    |
| \( \text{PbOH}^+ \)        | \( \text{Pb}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{PbOH}^+ + \text{H}^+ \)             | (51) -7.71     |
| \( \text{PbSO}_4 \)       | \( \text{Pb}^{2+} + 2\text{SO}_4^{2-} \leftrightarrow \text{PbSO}_4 \)                           | (52) 2.69      |
| \( \text{Pb(OH)}_2(s) \)   | \( \text{Pb}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Pb(OH)}_2(s) + 2\text{H}^+ \)       | (53) -13.6     |
| \( \text{PbO} \)          | \( \text{Pb}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{PbO} + 2\text{H}^+ \)             | (54) -12.9     |
| \( \text{PbSO}_3(s) \)    | \( \text{Pb}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{PbSO}_3(s) \)                        | (55) 7.79      |
| \( \text{Pb(CO}_3^{2-} \) | \( \text{Pb}^{2+} + 2\text{H}_2\text{O} + 2\text{CO}_2 \leftrightarrow \text{Pb(CO}_3^{2-} + 4\text{H}^+ \) | (56) -23.26    |
| \( \text{PbCO}_3 \)       | \( \text{Pb}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{PbCO}_3 + 2\text{H}^+ \) | (57) -10.08    |
| \( \text{PbCO}_2\text{OH}^- \) | \( \text{Pb}^{2+} + 2\text{H}_2\text{O} + 2\text{CO}_2 \leftrightarrow \text{PbCO}_2\text{OH}^- + 3\text{H}^+ \) | (58) -18.48    |
| \( \text{PbHCO}_3^- \)    | \( \text{Pb}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{PbHCO}_3^- + \text{H}^+ \)  | (59) -3.33     |
| \( \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2(s) \) | \( 3\text{Pb}^{2+} + 3\text{H}_2\text{O} + 2\text{CO}_2 \leftrightarrow \text{Pb}_3(\text{CO}_3)_2(\text{OH})_2(s) + 6\text{H}^+ \) | (60) -13.96    |
| \( \text{PbCO}_3(s) \)    | \( \text{Pb}^{2+} + \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{PbCO}_3(s) + 2\text{H}^+ \) | (61) -3.48     |

Note: 1. \( K \) data obtained from HSC Chemistry® 6.0 database.

\[
\begin{align*}
\text{Ca}^{2+} + \text{Ca(OH)}_2(s) + \text{CaOH}^+ &= \text{Ca}^{\text{total}} \\
2 \times \text{Ca}^{2+} + \text{CaOH}^+ &= \text{Ca}^{\text{total}} \\
\text{Ca}^{\text{total}} &= \text{Ca}^{\text{total}} \\
\text{CaCO}_3(s) + \text{CaCO}_3 + \text{CaHCO}_3 + \text{Ca}^{2+} &= \text{Ca}^{\text{total}} \\
\text{CaCO}_3 + \text{CaHCO}_3 + \text{CaCO}_3 + \text{H}_2\text{CO}_3 + \text{Ca}^{2+} + \text{CaCO}_2(g) &= \text{CaCO}_3^{\text{total}} \\
\text{CaHCO}_3 + \text{H}_2\text{CO}_3 + 2(\text{H}_2\text{CO}_3 + \text{CaCO}_3 + \text{CaCO}_2(g)) &= \text{CaHCO}_3^{\text{total}}
\end{align*}
\]

Figure 1. Calculated species distributions of 30 mM Ca(OH)\(_2\) at different pH: (a) with log concentration vs. pH; (b) with fraction of calcium vs. pH.

Figure 2. Calculated species distributions of 10 mM CaCO\(_3\) at different pH: (a) with log concentration vs. pH; (b) with fraction of calcium vs. pH.
The equilibrium pH of the mixture is 12.42 with the concentration of SO$_4^{2-}$ being 8.668 mM. Based on these data, the removal ratio of SO$_4^{2-}$ can be calculated and shown in Table 3.

According to the ICP-OES measurement results, the concentration of SO$_4^{2-}$ in the spent electrolyte sample was 1.53 M. Figure 4 shows the reaction equilibriums of 1.53 M SO$_4^{2-}$ reacting with 1.55 M Ca(OH)$_2$.
Ca(OH)\textsubscript{2} at different pH. Extra Ca(OH)\textsubscript{2} was introduced to ensure the removal of SO\textsubscript{4}\textsuperscript{2\textendash} ions. As can be seen from Figure 4, the main precipitates were CaSO\textsubscript{4}·2H\textsubscript{2}O in a wide pH range (pH: 2~12), according to Equation (9), and when pH < 2 [19], CaSO\textsubscript{4}·2H\textsubscript{2}O would dissolve into the solution and become Ca\textsuperscript{2\textendash} and SO\textsubscript{4}\textsuperscript{2\textendash} ions, according to Equation (10). At the same time, if pH > 12, the ratio of CaSO\textsubscript{4}·2H\textsubscript{2}O might also decrease because of the formation of Ca(OH)\textsubscript{2} (Figure 4c) and SO\textsubscript{4}\textsuperscript{2\textendash} (Figure 4b), according to Equation (11). The final pH and composition of the mixture are shown in Table 3; as can be seen, the equilibrium pH of the mixture is 12.42 with C\textsubscript{Ca\textsuperscript{2\textendash}} = 25.06 mM, C\textsubscript{SO\textsubscript{4}\textsuperscript{2\textendash}} = 8.668 mM, and C\textsubscript{CaSO\textsubscript{4}·2H\textsubscript{2}O} = 1517 mM. Based on these data, the removal ratio of SO\textsubscript{4}\textsuperscript{2\textendash} can be calculated and shown in Table 3. Also, by comparing the data obtained from the precipitation process with the saturated CaCO\textsubscript{3} and CaSO\textsubscript{4} solution data, the result indicates that if CO\textsubscript{2} was introduced in the precipitation process, the removal efficiency of SO\textsubscript{4}\textsuperscript{2\textendash} might decrease. Therefore, ambient CO\textsubscript{2} should be avoided in the precipitation process to obtain a higher removal efficiency. Also, the theoretical results obtained in this model are very close to the experimental results of Fang et al. [23].

\[
\text{Ca(OH)\textsubscript{2}}(s) + \text{H}_2\text{SO}_4 \leftrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} (s) \tag{9}
\]

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} (s) + \text{H}^+ \leftrightarrow \text{HSO}_4^- + \text{Ca}^{2\textendash} + 2\text{H}_2\text{O} \tag{10}
\]

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} (s) + 2\text{OH}^- \leftrightarrow \text{Ca(OH)\textsubscript{2}}(s) + \text{SO}_4\textsuperscript{2\textendash} + 2\text{H}_2\text{O} \tag{11}
\]

**Figure 4.** Calculated species distributions of 1.53 M SO\textsubscript{4}\textsuperscript{2\textendash} reacting with 1.55 M Ca(OH)\textsubscript{2} at different pH: (a) with log concentration vs. pH; (b) with fraction of sulfate vs. pH; (c) with fraction of calcium vs. pH.
Table 3. Calculated equilibrium species distributions of the precipitation process and carbonation process, with and without filtration.

| Contents                               | Species        | Concentrations (mM) | Removal Efficiency of SO$_4^{2-}$/Pb$^{2+}$ |
|----------------------------------------|----------------|---------------------|---------------------------------------------|
| 1.55 M Ca(OH)$_2$ + 1.53 M SO$_4^{2-}$ | OH$^-$         | 26.53               |                                             |
|                                        | CaOH$^+$       | 3.605               |                                             |
|                                        | CaSO$_4$       | 4.457               |                                             |
|                                        | Ca$^{2+}$      | 25.06               |                                             |
|                                        | SO$_4^{2-}$     | 8.668               |                                             |
|                                        | CaSO$_4$2H$_2$O| 1517                |                                             |
|                                        | Pb(OH)$_2$     | $3.447 \times 10^{-4}$ |                                             |
|                                        | Pb(OH)$_3^{-}$ | $1.416 \times 10^{-2}$ |                                             |
| Carbonation after filtration at pH 7 (0.1 M CO$_2$) | Ca$^{2+}$      | 0.4509              | 99.15%                                      |
|                                        | SO$_4^{2-}$     | 13.01               |                                             |
|                                        | CaSO$_4$       | 0.1118              |                                             |
|                                        | HCO$_3^-$      | 57.32               |                                             |
|                                        | CaCO$_3$(s)    | 32.44               |                                             |
|                                        | PbCO$_3$(s)    | $1.397 \times 10^{-2}$ |                                             |
|                                        | PbCO$_3^+$     | $2.512 \times 10^{-4}$ | 96.35%                                      |
|                                        | PbHCO$_3^-$    | $1.834 \times 10^{-4}$ |                                             |
|                                        | Pb(CO$_3$)$_2^{2-}$ | $7.332 \times 10^{-5}$ |                                             |
| Carbonation without filtration at pH 7 (0.1 M CO$_2$) | CaSO$_4$       | 4.457               | 69.61%                                      |
|                                        | HCO$_3^-$      | 20.48               |                                             |
|                                        | Ca$^{2+}$      | 4.098               |                                             |
|                                        | SO$_4^{2-}$     | 460.43              |                                             |
|                                        | CaCO$_3$(s)    | 476.2               |                                             |
|                                        | CaSO$_4$2H$_2$O| 1065                |                                             |

Figure 5 shows the distributions of lead-related ions at different pH. As can be seen from Figure 5a, no precipitation was formed in the whole pH range due to the extremely low concentration of lead and the existence of SO$_4^{2-}$ (Table 3). [28] This might be in favor of the precipitation process due to the fact that lead is toxic, and according to this simulation, no lead was precipitated in the precipitation process with Ca(OH)$_2$. Figure 5b shows the fraction of lead at different pH, based on which the distribution of lead can be divided into three regions: at low pH region (pH < 2), the main form of lead is Pd$^{2+}$; at moderate pH region (2 < pH < 7), lead was mainly in the form of PbSO$_4$ (Equation (52) from Table 1); at high pH region (pH > 7), lead forms a complex with OH$^-$ ions and forms four kinds of complexes with the increase of pH (Equations (48)–(51) from Table 1).

![Figure 5](image-url)

**Figure 5.** Calculated species distributions of 8.67 mM SO$_4^{2-}$ reacting with 0.0145 mM Pb$^{2+}$ at different pH: (a) with log concentration vs. pH; (b) with fraction of lead vs. pH.
3.2. Carbonation

After the precipitation process, the extra Ca(OH)\textsubscript{2} should be removed and the carbonation process introduced to both remove extra Ca(OH)\textsubscript{2} and neutralize the solution. Due to the fact that the appearance of CO\textsubscript{2} might promote the production of CaCO\textsubscript{3}, which in turn might influence the final products of the carbonation process, the carbonation process was divided into 2 scenarios: with filtration and without filtration of the precipitates resulted from the precipitation process, respectively. In the filtration and carbonation scenario, the total calcium concentration (\(T_{Ca}\)) \(T_{Ca} = C_{Ca^{2+}} + C_{CaOH^{+}} + C_{CaSO_{4}} = 33.122\) mM, while the total sulfate concentration (\(T_{SO_{4}^{2-}}\)) \(T_{SO_{4}^{2-}} = C_{SO_{4}^{2-}} + C_{CaSO_{4}} = 13.125\) mM. Figure 6 shows the calculated species distributions of the carbonation process after filtration; as can be seen, the main precipitate when pH > 6 was CaCO\textsubscript{3} (Equation (12)), while in the pH range of 3~5 the main precipitate was CaSO\textsubscript{4}·2H\textsubscript{2}O (Equation (43) from Table 1). As shown in Figure 6b, with the increase of pH the ratio of calcium in Ca\textsuperscript{2+} ion form decreases and the ratio in CaCO\textsubscript{3} form increases, which was caused by the formation of CaCO\textsubscript{3} in the alkaline region (Equation (12)). As can be seen from Figure 6c, when the pH > 7, the dominant species is SO\textsubscript{4}\textsuperscript{2-}, because the dissociation of CaSO\textsubscript{4} (Equation (13)) and the dissociation of CaSO\textsubscript{4} were caused by the constant removal of Ca\textsuperscript{2+} according to Equation (12). When the final pH is 7, the equilibrium species distributions are shown in Table 3; as can be seen, the equilibrium \(C_{Ca^{2+}} = 0.4509\) mM, \(C_{SO_{4}^{2-}} = 13.01\) mM, and the main precipitate was CaCO\textsubscript{3}(s) (32.44 mM).

\[
\begin{align*}
\text{Ca}^{2+} + \text{CO}_2 + 2\text{OH}^- & \leftrightarrow \text{CaCO}_3(s) + \text{H}_2\text{O} \\
\text{CaSO}_4 & \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-}
\end{align*}
\]

In the case of carbonation without filtration, the total calcium concentration is \(T_{ca} = 1.55\) M, and the total sulfate concentration is \(T_{SO_{4}^{2-}} = 1.53\) M. As can be seen from Figure 7, the dominant precipitated

---

**Figure 6.** Calculated species distributions of carbonation process with filtration at different pH: (a) with log concentration vs. pH; (b) with fraction of calcium vs. pH; and (c) with fraction of sulfate vs. pH.
species were CaSO₄·2H₂O (pH: 2−5, Equation (9)), CaSO₄·2H₂O and CaCO₃ (pH: 5−13, Equations (9) and (12)), and Ca(OH)₂(s) and CaCO₃ (pH: 13−14, Equations (11) and (12)), respectively. When pH is smaller than 2, a certain amount of CaSO₄·2H₂O would dissolve, as can be seen from Figure 7b (Equation (10)). The decrease of C₅CaSO₄·2H₂O in pH 5−7 was mainly caused by the formation of CaCO₃ (Equation (12)), which leads to the dissolution of CaSO₄·2H₂O (Equation (14)), and simultaneously results in the increase of C₅SO₄²⁻ in the same region. In other words, this decrease of C₅CaSO₄·2H₂O in pH 5−7 resulted from the combination of CaSO₄·2H₂O dissolution reactions (Equation (14)) and carbonation reaction (Equation (12)). When pH is larger than 13, the fraction of CaSO₄·2H₂O further decreases to almost zero; this was caused by both the formation of CaCO₃ (Equation (12)), and most importantly, the formation of Ca(OH)₂(s) (Equation (11)) at extremely high pH. The fraction of CaSO₄·2H₂O decreases with the increase of CO₂ concentrations, according to Figure 7b–d. To obtain a higher removal ratio of SO₄²⁻, 0.1 M CO₂ was chosen. The equilibrium species distributions of the solution at pH 7 are listed in Table 3; the equilibrium C₅Ca²⁺ = 4.098 mM, C₅SO₄²⁻ = 460.43 mM, C₅CaCO₃(s) = 476.2 mM, and C₅CaSO₄·2H₂O = 1065 mM. The calculated removal ratio of sulfate, in this case, is lower (69.61%) than the carbonation after filtration (99.15%).

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \tag{14}
\]

Figure 7. Calculated species distributions of carbonation process without filtration at different pH: (a) C₅CO₂ = 0.1 M with log concentration vs. pH; (b) C₅CO₂ = 0.1 M with fraction of sulfate vs. pH; (c) C₅CO₂ = 1 M with fraction of sulfate vs. pH; and (d) C₅CO₂ = 2 M with fraction of sulfate vs. pH.

Since carbonation with filtration was a better option than carbonation without filtration, only carbonation with filtration was calculated for lead (Figure 8). As can be seen from Figure 8a, the PbCO₃(s) precipitate (Equation (61) from Table 1) existed in the moderate pH region (5 < pH < 9); when pH is lower than this value PbCO₃(s) might react with H⁺ to form PbHCO₃⁺, according to
Equation (15), while at a higher pH with the increase of pH, PbCO$_3$(s) might react with both CO$_3^{2-}$ and OH$^-$ to form Pb$_3$(CO$_3$)$_2$OH$_2$(s) (Equation (16)), Pb(CO$_3$)$_2^{2-}$ (Equation (17)), PbCO$_3$OH$^-$ (Equation (18)), and Pb(OH)$_3^{2-}$ (Equation (19)), respectively. The end pH = 7 was adopted for the carbonation process, in which 96.35% of lead was precipitated as PbCO$_3$(s), and thus stabilized with CaCO$_3$ in the carbonation process (Table 3).

$$\text{PbCO}_3(s) + \text{H}^+ \leftrightarrow \text{PbHCO}_3^+$$  \hspace{1cm} (15)

$$3\text{PbCO}_3(s) + 2\text{OH}^- \leftrightarrow 3\text{Pb}_3(\text{CO}_3)_2\text{OH}_2(s) + \text{CO}_3^{2-}$$  \hspace{1cm} (16)

$$\text{PbCO}_3(s) + \text{CO}_3^{2-} \leftrightarrow \text{Pb(}_3\text{CO}_3)_2^{2-}$$  \hspace{1cm} (17)

$$\text{PbCO}_3(s) + \text{OH}^- \leftrightarrow \text{PbCO}_3\text{OH}^-$$  \hspace{1cm} (18)

$$\text{PbCO}_3(s) + 3\text{OH}^- \leftrightarrow \text{Pb(OH)}_3^{2-} + \text{CO}_3^{2-}$$  \hspace{1cm} (19)

![Figure 8](image_url)

**Figure 8.** Calculated lead related species distributions of carbonation process with filtration at different pH: (a) C$_{\text{CO}_2}$ = 0.1 M with log concentration vs. pH; and (b) C$_{\text{CO}_2}$ = 0.1 M with fraction of lead vs. pH.

4. Conclusions

Normally, the spent LAB electrolytes can be directly filtered and reused on the condition that the electrolytes were collected and handled properly in the dissembling plant. For dissembling plants without appropriate collecting setups, electrolytes are often polluted with foreign ions, since electrolytes are often discharged onto the ground directly. These polluted electrolytes cannot be purified by simple filtration, and thus require more reasonable recycling techniques. Instead, it is more reasonable and profitable to recycle and stabilize SO$_4^{2-}$ in the form of CaSO$_4$.2H$_2$O, which can be widely used as a fertilizer and for building materials. In this study, the polluted electrolyte sample was recycled with chemical precipitation and carbonation techniques. To understand the whole recycling process, thermodynamic simulations in the precipitation and carbonation processes were conducted. The thermodynamic calculations of saturated Ca(OH)$_2$, CaCO$_3$, and CaSO$_4$ solutions helped us to understand the whole process, since Ca(OH)$_2$ and CaSO$_4$ appear in both precipitation and carbonation processes when the pH is higher than 13. Additionally, CaCO$_3$ appears in the carbonation process with and without filtration. The theoretical limit for the removal ratio of SO$_4^{2-}$ was predicted to be 99.15% with 1.53 M SO$_4^{2-}$ and 1.55 M Ca(OH)$_2$. Also, by comparing the carbonation process with and without pre-filtration of the precipitates obtained from the precipitation process, the theoretical removal efficiency of SO$_4^{2-}$ was calculated to be 99.15% and 69.61%, respectively. With the increase of CO$_2$ concentrations in the solution, the removal efficiency of SO$_4^{2-}$ further decreased. Furthermore, the chemical precipitation and carbonation of lead in the spent electrolyte sample were calculated; no precipitation existed in the precipitation process due to the appearance of SO$_4^{2-}$, while 96.35% of lead was precipitated as PbCO$_3$(s) in the carbonation process, which stabilized lead with CaCO$_3$. The thermodynamic calculations helped us to design and understanding the whole removal process quantitatively. Based on the thermodynamic calculation results, the optimized removal process of
SO$_4^{2-}$ should be precipitation without contact with ambient CO$_2$, since PbCO$_3$ might precipitate around pH 9, which would lead to the existence of lead in CaSO$_4$·2H$_2$O. Additionally, filtration should be undertaken before the carbonation process to avoid the re-dissolution of CaSO$_4$·2H$_2$O. After filtration, the final product of the recycling process (CaSO$_4$·2H$_2$O) is obtained. In the following carbonation process, the flow rate of CO$_2$ and pH should be controlled properly to stabilize lead and extra calcium in the form of PbCO$_3$ and CaCO$_3$, respectively. At last, after chemical precipitation and carbonation, there is still around 13 mM SO$_4^{2-}$ in the solution, which needs to be removed by adsorption or ion-exchange techniques. The overall theoretical chemical precipitation limit for removal of SO$_4^{2-}$ was 99.15%. The limitation of the simulation was: (1) in the simulation process of carbonation, where the system was assumed to be a closed system with all CO$_2$ dissolved in the solution; and (2) equilibrium at each pH is achieved by both carbonation reaction and addition of HCl or NaOH when needed. These limitations might cause the deviation of simulation values from experimental results, however, the tendency of the whole process should be similar, which makes the simulation of the carbonation process a good tool for reference.

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