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A Feasible Route for Preparation of Calcium Sulfate Whiskers from FGD Gypsum via Filtrate Recycle under Hydro-Thermal Conditions

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Abstract: Calcium sulfate whiskers (CSWs) were synthesized using purified flue-gas desulfurization (FGD) gypsum as raw materials using a hydrothermal method, where the filtrate was recycled back to the reaction slurry. The study investigated the impact of pH and Cu^{2+} concentration in the reaction solution with or without reagent compensation. The effects of cycle number on the crystal morphology, phase structure, and productivity of the hydrothermal products were also examined. The findings indicate that the crystal morphology and quality of the CSWs deteriorated as the cycle number increased due to a rise in pH and a decrease in Cu^{2+} concentrations in the reaction solution without reagent compensation. However, adding a specific amount of H_2SO_4 and $CuCl_2$ to the slurry with filtrate recycle maintained the long fibrous shape of the hydrothermal products for up to seven cycles while also increasing their productivity from 73.7% to 86%. Regardless of reagent compensation, the cycle number of filtrate significantly affected the crystal morphology of the hydrothermal products, but it had no impact on their phases.

Keywords: FGD gypsum; calcium sulfate whisker; hydrothermal method; filtrate recycle; cleaner production

1. Introduction

The exceptional performance and wide-ranging applications of calcium sulfate whiskers (CSWs) have resulted in increased attention toward controlling crystal morphology during their preparation [1–8]. Hydrothermal methods have enabled the synthesis of calcium sulfate whiskers (CSWs) with an aspect ratio of approximately 98 from high-quality natural gypsum [9,10]. With increasing emphasis on environmental protection and the growing utilization of industrial solid waste resources, research efforts have shifted toward exploring the use of industrial by-product gypsum (such as flue-gas desulfurization (FGD) gypsum and phosphogypsum) in the preparation of CSWs with a high aspect ratio using hydrothermal techniques. This area of research has become a current focus due to its potential for sustainable and efficient production of CSWs [1,11–13].

The composition of the solution plays a significant role in the hydrothermal synthesis of calcium sulfate whiskers (CSWs) from flue-gas desulfurization (FGD) gypsum, and incorporating crystal modifiers into the reaction solution to enhance the crystallization of CSWs is a promising approach to increase their aspect ratios [14–20]. Certain metal ions (such as Na^+, K^+, Mg^{2+}, Cu^{2+}, Fe^{3+}, and Al^{3+}) and organic additives have demonstrated significant effects on the crystal morphology and sizes of CSWs [7,14,21–27]. At specific concentrations, the presence of Na^+, K^+, or Cu^{2+} has been shown to enhance the aspect ratio of CSWs [7,14,18]. However, Mg^{2+} and Fe^{3+} have been linked to shorter lengths

of CSWs, and Al^{3+} concentrations above 2.5×10^{-3} $mol \cdot L^{-1}$ have resulted in comparable outcomes [25,26]. Organic additives, such as sodium dodecyl sulfonate and sodium dodecyl benzene sulfonate, exhibit different binding energies on distinct crystal faces of CSWs, with (002) displaying the highest binding energy, leading to a decline in the growth of CSWs along (002) [27]. Generally, the substitution of Ca^{2+} with metal ions or their selective adsorption onto different facets can alter the crystal morphology and growth of CSWs [23–27].

Compared with inorganic additives, inorganic additives lack the functional groups of organic reagents and cannot chemically adsorb gypsum crystals; thus, not affecting the crystal morphology of gypsum crystals. However, in the reaction solution, the concentration, valence state, radius, and structure of anions and cations introduced by the solution of inorganic salts exhibit different characteristics. This results in the possibility of selective adsorption, substitution, and doping of anions and cations on different crystal faces of hemihydrate gypsum crystals. Additionally, inorganic additives are more cost-effective than organic additives, which is beneficial for reducing production costs.

Hydrothermal methods are widely used for the preparation of CSWs, with reported investigations mainly focusing on controlling crystal morphology and size under varying conditions, and their crystallization mechanism. According to classical nucleation theory, the formation of gypsum crystals undergoes the two stages of nucleation and growth. Ca^{2+} and SO_4^{2-} would be generated because of the dissolution of FGD gypsum, and then calcium sulfate hemihydrate (HH) would be formed under solution conditions. For gypsum crystals, their micromorphology and structure are closely related to both their own crystallization habits and their growth environment. Hence, the nucleation and growth of HH would be affected by the process conditions, such as temperature, pH, and the concentration of additives [28–30]. EI Hall et al. studied the effects of cetylammonium pyridine chloride (CPC) on gypsum crystallization and found that the free energy of gypsum nucleation would decrease with the increase in supersaturation of Ca^{2+} and SO_4^{2-} in reaction solution [31]. Lancia et al. [32] and Massaro et al. [33] believed that the induction time required for nucleation was mainly influenced by factors such as temperature, solution supersaturation, and ionic bond strength.

However, to our knowledge, there have been no studies on the reuse of the filtrate produced during CSW preparation via hydrothermal methods. The filtrate from CSW preparation using FGD gypsum as a raw material contains metal ions, organic additives, and H_2SO_4 [7,14,18]. Discharging this filtrate without proper treatment poses a risk to the environment. However, the cost of treatment makes the industrial production of CSWs from FGD gypsum via hydrothermal methods uneconomical. Therefore, developing a controllable and cost-effective method for preparing CSWs from FGD gypsum via filtrate recycling at hydrothermal conditions would be of interest and could aid in the cleaner production of CSWs.

It has been reported that $CuCl_2$ can effectively serve as a crystal modifier to enhance the crystal morphology of calcium sulfate whiskers (CSWs) and increase their aspect ratios [9,13]. In this study, $CuCl_2$ was used as a crystal modifier, while H_2SO_4 was used to adjust the pH of the reaction solution. CSWs were prepared under various hydrothermal recycle conditions of the filtrate, and their morphology, phase, chemical composition, and productivity were characterized. Specifically, the study aimed to investigate the effects of the cycle number of the filtrate on the crystallization, quality, and productivity of CSWs, and to explore the changes in the pH and Cu^{2+} concentration of the solution before and after the reaction. This study provides an environmentally friendly, controllable, and cost-effective approach for the preparation of CSWs using recycled filtrate under hydrothermal conditions.

2. Materials and Methods

Analytical grade H_2SO_4 and $CuCl_2$ were procured from Luoyang Chemical Reagent Co. Ltd., located in Luoyang, China. The FGD gypsum used in this study was obtained

from a power plant in Henan, China, and was subjected to purification procedures, resulting in a $CaSO_4 \cdot 2H_2O$ content of approximately 95% by weight. [14,34].

The slurry containing a specific amount of H_2SO_4 and copper chloride was transferred into a double-walled jacket autoclave and maintained at 120–140 °C for 40–90 min. The resulting suspension was then filtered, washed, and dried for 4 h at 80–100 °C [7]. After filtration, the filtrate was clarified and reused directly back into the slurry without any reagent compensation. The pH and Cu^{2+} concentration of the solution was analyzed to investigate their changes before and after the reaction. The crystal morphology, phase, and productivity of the CSWs produced after each cycle were also analyzed to determine the effects of the cycle numbers of the filtrate on these parameters. The experimental procedure is presented in Figure 1.
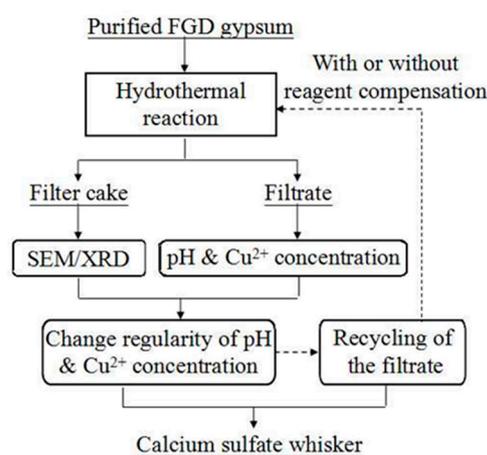

Figure 1. Experimental procedure.

To perform a comparison, specific amounts of H_2SO_4 and $CuCl_2$ were added to the filtrate to compensate for any losses, and the compensated filtrate was repeatedly recycled into the reaction slurry until the crystal morphology of CSWs deteriorated significantly. The experimental procedures were briefly depicted in Figure 1. In this study, the filtrate produced from the original reaction was denoted as "N_0". "N_i" represented the filtrate that was recycled "i times" without any reagent compensation, while "$N_{r\text{-}i}$" represented the filtrate that was recycled "i times" with reagent compensation.

The crystal morphology of the hydrothermal products was observed using scanning electron microscopy (SEM; Quanta 450, FEI, Hillsoboro, OR, USA), and their phase structures were examined using powder X-ray diffraction (XRD) with an X'Pert PRO X-ray diffractometer (Philips, PANalytical B.V., Almelo, The Netherlands). The chemical compositions of the samples were analyzed using a wavelength-dispersive X-ray fluorescence spectrometer (XRF; Magix PW2403, PANalytical B.V., Almelo, The Netherlands). The pH values of the slurry before the reaction and the filtrate after the reaction were measured with a pH meter (pH-200, HM, Seoul, Republic of Korea). The Cu^{2+} concentration of the filtrate was determined using an atomic absorption spectrometer (AAS; novAA400P, Analytik Jena, Jena, Germany), and the test methods followed the Chinese GB 7475-87 (Water Quality-Determination of Copper, Zinc, Lead and Cadmium-Atomic Absorption Spectrometry) protocol. The percentage change in the pH value and Cu^{2+} concentration were calculated using Equation (1), where w_0 is the pH value or Cu^{2+} concentration in solution before the reaction, and w_i is the pH value or Cu^{2+} concentration of the filtrate recycled "*i*" times:

$$Y = \frac{w_0 - w_i}{w_0} \times 100\% \tag{1}$$

The productivity of CSWs was determined using Equation (2), where it was assumed that there was no significant loss of CSWs during the entire process. The molecular weight ratio of calcium sulfate dihydrate (DH) and α-calcium sulfate hemihydrate (α-HH) was

1.18621. M_0 represented the weight of the purified FGD gypsum added into the reaction slurry, and M_i was the weight of the obtained CSWs after the reaction for "i" cycles. P represented the content of DH in the purified FGD gypsum, which was 95% in this study:

$$G = 1.18621 \times \frac{M_i}{P \times M_0} \times 100\% \tag{2}$$

3. Results and Discussion

3.1. Effect of Filtrate Recycle Number on Preparation CSWs without Reagent Compensation

Figure 2 shows SEM images of the CSWs prepared using filtrate at different cycle numbers without reagent compensation under hydrothermal conditions. As shown in Figure 2a, CSWs with a fibrous morphology, smooth surface, and a larger average aspect ratio were prepared using FGD gypsum as a raw material under hydrothermal conditions. However, when the recycled filtrate without reagent compensation was used to prepare CSWs for the first time, the length and distribution of the CSWs were significantly decreased, as shown in the SEM images of the samples in Figure 2b. Furthermore, when the filtrate was recycled for the third time, the crystallization of the CSWs was significantly worsened, and almost no CSWs were detected in the hydrothermal products, as shown in Figure 2d. These results suggest that the cycle number had a significant effect on the crystal morphology of the CSWs prepared from FGD gypsum.
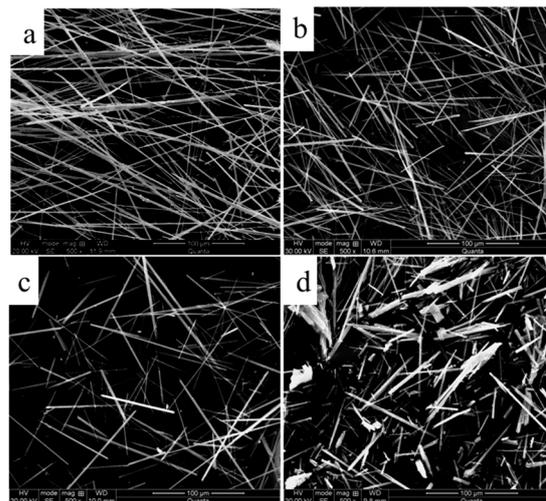

Figure 2. SEM images of the CSWs prepared by using filtrate at different cycle numbers without reagent compensation under hydrothermal conditions (**a**) N_0, (**b**) N_1, (**c**) N_2, and (**d**) N_3.

To gain insight into the effect of filtrate cycle number on CSWs preparation without reagent compensation, it is essential to consider the changes in the solution compositions after each reaction. Such changes can be inferred from alterations in the concentration of the crystal modifier and the pH of the solution. Therefore, to investigate the impact of the filtrate cycle number on CSWs preparation without reagent compensation, we analyzed the pH and Cu^{2+} concentration of the filtrate at different cycles.

The changes in the pH value of the filtrate at different cycle numbers were depicted in Figure 3. The pH of the filtrate without reagent compensation gradually increased by about 28% with an increase in the cycle number. It is worth noting that previous research on purified FGD gypsum chemical components analysis showed that the presence of 5% impurities, which were often stable in the form of fly ash, could not be easily removed by acid treatment at ambient temperature [34,35]. However, these impurities could react with H_2SO_4 at elevated temperatures, leading to the consumption of H^+ in the solution [36]. This finding is consistent with the results shown in Figure 3, where the pH of the filtrate increased gradually with further increases in the cycle number for preparing CSWs without

reagent compensation. It is also worth mentioning that the crystal morphology of CSWs would worsen with the increasing pH of the solution.
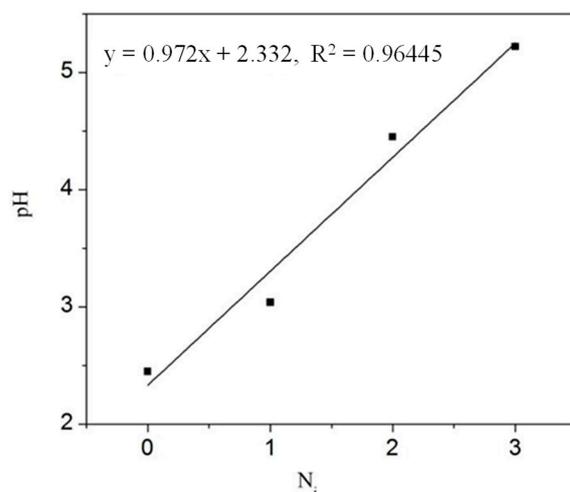

Figure 3. pH of the filtrate changes versus the cycle numbers without reagent compensation under hydrothermal conditions.

The product characteristics of α-HH crystals prepared using FGD gypsum with the hydrothermal method were found to be strongly affected by the solution pH, with decreasing initial pH values leading to smaller crystal sizes [37]. The pH exerts its influence on the dehydration of FGD gypsum primarily by affecting the degree of super-saturation [38]. As the pH of the solution increases, the super-saturation of the reaction solution decreases, resulting in a lower nucleation rate under higher pH conditions. Particle size is determined by both nucleation and crystal growth rates [39], with a low-nucleation rate leading to the formation of a small number of nuclei, which then have a higher probability of growing into large crystals. Consequently, an increase in pH leads to an increase in crystal size. Without reagent compensation, the pH of the solution increases after the reaction, while the solubility product of calcium sulfate decreases due to the decrease in the super-saturation of the reaction solution and the nucleation rate of CSWs.

The Cu^{2+} concentration of filtrate without reagent compensation was found to decrease gradually with increasing cycle number, as illustrated in Figure 4. The high aspect ratio of CSWs in an aqueous solution is attributed to the interaction between liquid water and the crystal's side faces, which inhibits radial growth [40]. In the crystallization process of CSWs, four dominant faces (0 0 1), (1 1 0), (−1 1 0), and (2 0 0) are present. Face (1 1 0) is composed of Ca^{2+} and SO_4^{2-}, and Cu^{2+} is known to adsorb onto this crystal face, further inhibiting radial growth and promoting the formation of whiskers with higher aspect ratios [41]. Previous studies have shown that Cu^{2+} can chemically adsorb onto these crystal faces to form a $CuSO_4$ film, and can even replace Ca^{2+}, hindering radial growth and promoting aspect ratios [42,43]. Therefore, the adsorption of Cu^{2+} onto CSWs crystal planes and the substitution of Ca^{2+} by Cu^{2+} contribute to the decrease in Cu^{2+} concentration when filtrate is recycled without reagent compensation.

3.2. Effect of Filtrate Cycle Number on Preparation CSWs with Reagent Compensation

Previous studies have indicated that the concentration of H_2SO_4 and $CuCl_2$ significantly influences the transformation kinetics and time from FGD gypsum to CSWs. Specifically, increasing the H_2SO_4 concentration and decreasing the $CuCl_2$ concentration can reduce the nucleation and growth stages, resulting in a larger driving force that promotes the transformation from FGD gypsum to CSWs [44]. Furthermore, the presence of both sulfuric acid and copper chloride in the reaction solution can stabilize the concentration of Ca^{2+} and enhance the crystallization of CSWs [42]. Therefore, proper reagent compensation of H_2SO_4 and $CuCl_2$ is crucial for ensuring the quality of CSWs.
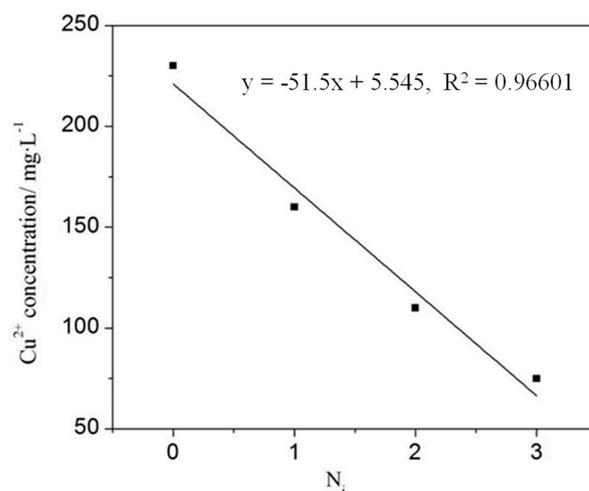
Figure 4. Cu^{2+} concentration of the filtrate changes versus the cycle numbers without reagent compensation under hydrothermal conditions.

In order to determine the compensation amount of the reagent, the variations of the reaction solution's pH and Cu^{2+} concentration with increasing contact time were also studied, as shown in Figure 5. According to Figure 5a, it can be observed that the pH of the solution gradually increases as the reaction progresses. In the initial stages of the reaction, the pH of the solution increases rapidly, but in the later stages, the rate of pH increase slows down until it reaches a relatively stable value. As shown in Figure 5b, the Cu^{2+} concentration gradually decreases with increasing reaction time and eventually stabilizes. The patterns of pH and Cu^{2+} concentration changes in the reaction solution provide a basis for reagent compensation.
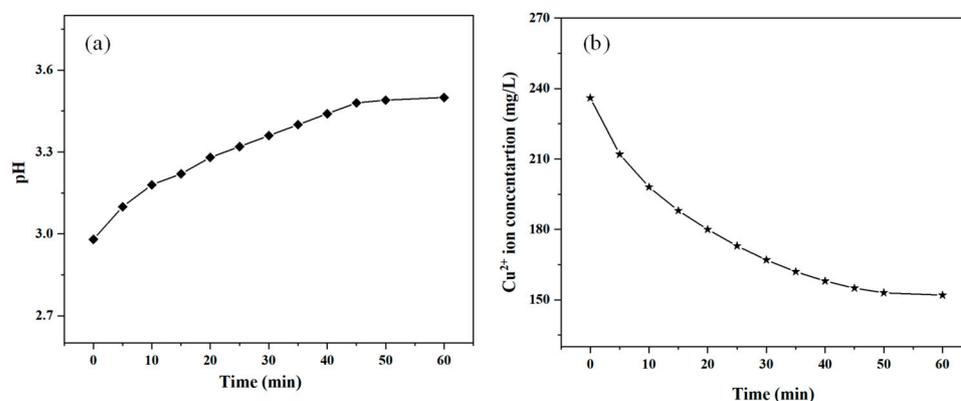

Figure 5. The pH and Cu^{2+} concentration of the filtrate with increasing contact time: (**a**) The variations of the filtrate's pH with increasing contact time, (**b**) Cu^{2+} concentration of the filtrate with increasing contact time.

Moreover, by analyzing the changes in pH and Cu^{2+} concentration before and after the reaction, it is possible to recycle the filtrate continuously with appropriate reagent compensation, provided that the quality of the CSWs is not compromised. This approach can effectively reduce the production cost of CSWs and minimize environmental impact. To further optimize the process, it is crucial to investigate the impact of filtrate recycling with reagent compensation at different cycle numbers on the crystal morphology of the products and their productivity.

The pH and Cu^{2+} concentration changes in the filtrate before and after the reaction were measured at different cycle numbers, and the results are presented in Table 1. The pH and Cu^{2+} concentration of the subsequent reaction solution were adjusted to their initial values by adding a certain amount of H_2SO_4 and $CuCl_2$, in accordance with the change

values of pH and Cu^{2+} concentration of the filtrate. The initial pH and Cu^{2+} concentration of the solution before the reaction were 2.46 and 236 mg/L, respectively. After the reaction, the pH values increased, with an average value of 3.10, while the Cu^{2+} concentrations decreased, with an average decrease of 31.5%. These results are consistent with the change patterns shown in Figures 3 and 4.

Table 1. pH and Cu^{2+} concentration changes percentage degree (Y) of the filtrate versus cycle numbers with reagent compensation under hydrothermal conditions.

Sample	N_{r-1}	N_{r-2}	N_{r-3}	N_{r-4}	N_{r-5}	N_{r-6}	N_{r-7}	N_{r-8}	N_{r-9}	N_{r-10}
pH	3.1	2.98	3.12	3.12	3.22	3.12	3.1	3.08	3.08	3.12
Y_1/%	26.5	21.6	27.3	27.3	31.4	27.3	26.5	25.7	25.7	27.3
Cu^{2+} concentration/mg·L^{-1}	161	163	159	165	158	160	163	158	164	165
Y_2/%	31.8	30.9	32.5	30.1	33.1	32.2	30.9	33.1	30.5	30.1

Notes: Y_1—percentage degree in pH value decrease each cycle; Y_2—percentage degree in Cu^{2+} concentration value decrease each cycle.

The SEM images of the samples prepared at different cycle numbers with reagent compensation are depicted in Figure 6. The crystal morphology of the CSWs was preserved after the filtrate was recycled three times with reagent compensation, as observed in Figure 6a,b. Even after seven cycles, the quality of the crystals did not significantly deteriorate, as shown in Figure 6c. However, after ten cycles, the length of the CSWs was considerably reduced, and their diameter coarsened, as demonstrated in Figure 6d. Consequently, the aspect ratio of the CSWs decreased, and the quality deteriorated. The excessive number of filtrate cycles and the accumulation of impurities in the reaction solution might be the reasons for the reduction in CSW's quality. In summary, the cycle number of the filtrate did not have significant effects on the crystal morphology of the hydrothermal products up to seven cycles.
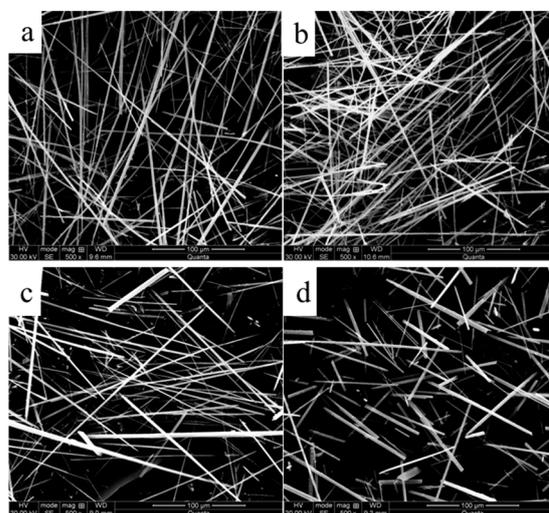

Figure 6. SEM images of the CSWs prepared by using filtrate at different cycle numbers with reagent compensation under hydrothermal conditions (**a**) N_{r-1}, (**b**) N_{r-3}, (**c**) N_{r-7}, and (**d**) N_{r-10}.

Figure 7 shows the XRD patterns of the samples prepared with reagent compensation at different cycle numbers. The diffraction peaks observed at 2θ values of 14.7, 25.5, and 31.7° (PDF#45-0848) indicated that the hydrothermal products at different cycle numbers were mainly composed of α-HH. However, the characteristic diffraction peaks of the hydrothermal products weakened as the cycle number increased, suggesting that the crystal growth was also affected. Therefore, while the cycle number of the filtrate did not affect the phase transformation from DH of purified FGD gypsum to α-HH of the

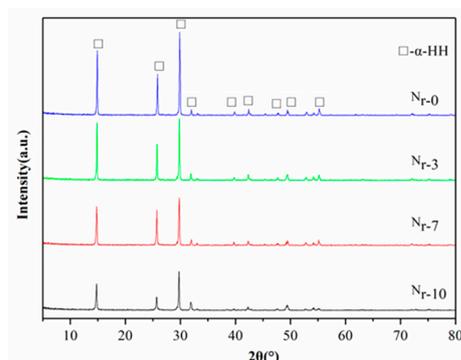hydrothermal products, it did weaken the crystal growth of CSWs, as confirmed by the SEM images in Figure 6.

Figure 7. XRD patterns of the CSWs prepared by using filtrate at different cycle numbers with reagent compensation under hydrothermal conditions.

Simultaneously, the chemical composition of the CSWs prepared at different cycle numbers with reagent compensation was analyzed to evaluate the phase transformation of the hydrothermal products, and the results are presented in Table 2. According to the theoretical composition of α-HH, its contents of SO_3 and CaO are 55.2 and 38.6 wt.%, respectively. Although the FGD gypsum used in the experiment was purified, it still contained about 5 wt.% impurities, which could result in a higher content of calcium oxide than the theoretical value [34]. It was observed that the content of sulfur trioxide in the hydrothermal products slightly increased and approached the theoretical value of α-HH with the increase in cycle number. This indicates that the hydrothermal products were mainly present as α-HH, and the cycle number had no effect on their phase structure.

Table 2. Chemical compositions of the samples prepared by using filtrate at different cycle numbers with reagent compensation under hydrothermal conditions.

Composition		SO_3	CaO	SiO_2	Fe_2O_3	Al_2O_3	MgO	CuO	K_2O	Others
	N_{r-0}	54.26	42.01	2.26	0.23	0.83	0.04	0.16	0.16	0.04
Content	N_{r-3}	54.61	42.01	2.10	0.22	0.66	0.05	0.14	0.18	0.02
(wt.%)	N_{r-7}	54.92	42.01	1.79	0.21	0.63	0.07	0.13	0.18	0.04
	N_{r-10}	55.00	42.40	1.78	0.16	0.38	0.04	0.09	0.14	0.01

Previous studies had shown that additives could be used to regulate the crystallization of hemihydrate gypsum in order to obtain the high aspect ratio and high-quality CSWs. However, as additives were added to the reaction solution, the solubility, nucleation induction time, and nucleation energy of gypsum crystals would be changed, which would affect the growth process and crystal morphology of CSWs. Moreover, the crystallization mechanism of CSWs would be lightly affected in different reaction solution systems. Therefore, in order to ensure the quality of CSWs prepared reusing filtrate under hydro-thermal conditions, the effects of filtrate cycle number on the productivity of CSWs were also necessarily studied in addition to the aforementioned micromorphology and phases.

3.3. Effect of Filtrate Cycle Number on the Productivity of CSWs

Table 3 shows the productivities of CSWs prepared at different cycle numbers. During the crystallization of CSWs from purified FGD gypsum, the gypsum underwent dissolution and recrystallization. The presence of certain metal ions can enhance the solubility of FGD gypsum and promote the crystal growth of CSWs [7]. As a result, some Ca^{2+} ions were dissolved in the reaction solution during the initial reaction, leading to the filtrate being in a saturated state and the productivity of CSWs being only 73.3%. However, when the filtrate was recycled as the reaction solution, the dissolution equilibrium was reached between

the reaction solution and the purified FGD gypsum, and only the concentrations of Ca^{2+} and SO_4^{2-} decreased due to nucleation and growth of the CSWs. The dissolution of FGD gypsum increased the amount of gypsum that could be converted into CSWs during the reaction, resulting in an increase in the productivity of CSWs from 73.7% in the original reaction to 86% when the filtrate was recycled six times. However, beyond a certain cycle number, the aspect ratio of the hydrothermal products decreased, and the number of tiny particles increased (Figure 6d). During filtration, these tiny particles were difficult to collect, resulting in an increase in mass loss and a decrease in the productivity of CSWs. Therefore, while recycling the filtrate to prepare CSWs can improve productivity, the cycle number should be optimized to maintain stable CSW quality and maximize productivity.

Table 3. Productivity of CSWs prepared by using filtrate at different cycle numbers with reagent compensation under hydrothermal conditions.

Samples	N_{r-0}	N_{r-1}	N_{r-2}	N_{r-3}	N_{r-4}	N_{r-5}	N_{r-6}	N_{r-7}	N_{r-8}	N_{r-9}	N_{r-10}
Productivity (%)	73.7	84.7	84.5	84.6	85.5	85.3	86.0	82.0	80.1	78.6	76.5

The filtrate obtained after the 7th cycle of use would be collected and processed using the sedimentation and filtration process. Subsequently, the pH value and Cu^{2+} concentration of the filtrate would be measured. This would allow for its reuse in the preparation of CSW with reagent compensation. However, it is necessary to conduct systematic research on this aspect.

4. Conclusions

CSWs were synthesized under hydrothermal conditions using FGD gypsum as a raw material and recycled filtrate as the reaction solution, with and without reagent compensation. The cycle numbers of the filtrate had a significant effect on the crystal morphology of the hydrothermal products, but had no effect on their phases. When the filtrate was recycled back to the slurry without reagent compensation, the crystal morphology and quality of the CSWs changed markedly as the cycle number increased, likely due to an increase in pH and a decrease in Cu^{2+} concentrations in the reaction solution. However, with reagent compensation—the addition of a certain amount of H_2SO_4 and $CuCl_2$ to the slurry with recycled filtrate—the crystal morphology of the hydrothermal products could still maintain a long fibrous shape up to seven cycles, and their productivity increased from 73.7% to 86%. The environmentally friendly, controllable, and feasible approach of reusing the filtrate as a reaction solution has great significance for the cleaner production of CSWs under hydrothermal conditions.

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Conflicts of Interest: The authors declare no conflict of interest.

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