Article

Recycling of Cement Kiln Dust as a Raw Material for Cement

Minhye Seo, Soo-Young Lee, Chul Lee and Sung-Su Cho *

Plant Engineering Center, Institute for Advanced Engineering, Yongin 17180, Korea; minhye_s@iae.re.kr (M.S.); sylee@iae.re.kr (S.-Y.L.); chullee0711@naver.com (C.L.)

* Correspondence: sungsu@iae.re.kr; Tel.: +82-31-330-7688

check for updates

Abstract: Cement kiln dust (CKD) is a major by-product of cement manufacturing and has the potential to be recycled as a raw material if the high concentrations of chlorine and potassium are removed. This study tested four leaching solutions (distilled water and three organic acids) and determined the optimum reaction conditions. At a liquid/solid (L/S ratio) of 10, the removal efficiency of formic, citric, and oxalic acid was higher than that of distilled water, but at L/S 20, distilled water also achieved a high removal efficiency of Cl ($\geq$90%) and K ($\geq$70%). In addition, to minimize the discharge of wastewater after leaching, the efficiency of ion-exchange resins for the recovery of leaching solution was tested. When the cation- and anion-exchange resins were arranged together, more than 95% of both Cl and K contained in the leaching solution could be removed. Leaching solution without Cl and K was found to have a high leaching efficiency even after being recycled three times, resulting in a significant reduction in wastewater emissions.

1. Introduction

Cement kiln dust (CKD) is a by-product of the cement manufacturing process and has traditionally been considered as an industrial waste product. Global cement production capacity in 2017 was ~4.99 billion tons per year [1,2], while the CKD production rate ranged from 54 to 200 kg per ton of produced cement clinker [3]. CKD is composed of fine, powdery solids and highly alkaline particulate material, and is similar in appearance to Portland cement. Its size distribution and chemical composition depends on production factors such as raw material, processing method, fuel, kiln type, cement type, and dust collection method (e.g., cyclones, bag filters, or electrostatic precipitators). Finer particles tend to exhibit a higher sulfate and alkali content. In general, CKD has a lower CaO and SiO_2 content than typical Portland cement (Table 1). Compared with cement, CKD is characterized by higher alkalis (especially potassium), and chloride. The high alkali content precludes the recycling of CKD into kilns, as this would exceed the maximum allowable value [4].

The increasing use of alternative fuels has driven a rise in chlorine input into kiln processes, increasing the importance of chlorine bypass systems in order to avoid operational problems. In particular, using waste fuel can increase the toxic metal content of the subsequent CKD [5]. A high chlorine content in CKD can lead to various problems in its reuse. In general, the maximum chloride content of cement is 0.10%, while the chloride contained in CKD may contain 0.35–15.4 wt%, depending on its raw materials [6]. Chlorine is highly corrosive, and high levels of it in cement can encourage steel corrosion. Several studies have reported that CKD can effectively improve soil strength and can be used as an alternative to lime for soil stabilization [6,7]. Its alkaline properties and good absorption capacity stabilize waste (instead of cement or lime) by reducing the moisture content and increasing the bearing capacity [8]. In addition to this, it has also been injected into an asphalt concrete mixture and

used as a mineral filler. However, CKD still contains corrosive substances such as chlorine, requiring a suitable technology to render them harmless.

Some cement plants simply send CKD to landfills, but the increasing annual stockpile of CKD and the high cost of its disposal requires an innovative solution that will allow CKD to be used in construction. Lanzerstorfer [9] reported that chloride concentration from cement kiln bypass dust (CKBD) depends on the particle size and can be removed by air classification. However, air classification is only a pretreatment and has the disadvantage of simultaneously requiring a leaching process. Thus, this study tested methods for the removal of chlorine and potassium ions from CKD in order to allow its reuse as a cement raw material, and evaluated the removal efficiency of various leaching conditions and the feasibility of recovering the leaching solutions through an ion-exchange system.

Table 1. Typical chemical composition of Portland cement and cement kiln dust (CKD).

Content	CaO	SiO$_2$	K$_2$O	Al$_2$O$_3$	Cl$^-$	Ref.
Portland cement (%)	64	22	0.3	5	<0.1	[6]
	63	20	-	5	-	[10]
	62	21	0.5	4	-	[11]
CKD (%)	38–50	11–16	3–13	3–6	0–5	[12]
	60.56	6.1	2.56	1.37	2.75	[13]

2. Materials and Methods

The CKD used in this study was obtained from Sampyo Cement, South Korea; it consisted mainly of CaO with significant amounts of chloride, potassium, and sulfate anions (Table 2). The Cl and K ions were leached using four agents: distilled water (DW) and the organic acids citric acid (99.5%, Daejung), oxalic acid (99.5%, Junsei), and formic acid (85%, Daejung). The reaction times (1–30 min) of each 200 mL distilled water (DW) and 0.5 M organic-acid leaching solution were compared. The leaching test of CKD was performed by changing the ratio of liquid and solid to 10 and 20. The CKD had a low specific gravity and had limitations in mixing and reacting in a liquid phase, making it difficult to further lower the L/S ratio. The removal efficiency of Cl$^-$ or K$^+$ ions can be estimated using the following Equation (1):

$$\text{Removal Efficiency (\%)} = \frac{\text{Leached Cl}^- \text{ (or K}^-)\text{conc. in CKD (g)}}{\text{Cl}^- \text{ (or K}^-)\text{conc. in CKD (g)}} \times 100 \tag{1}$$

The Cl and K ions leached from the CKD were configured in order to recycle the leaching solution through the ion-exchange reaction (Figure 1). An ion-exchange resin was used in conjunction with an ion-exchange resin (SAR20MBOH, Samyang Co., Ltd.) and cation-exchange resin (SCR-BH, Samyang Co., Ltd.), respectively. Then, the CKD (L/S: 20) was added to the deionized leaching solution through the ion-exchange resin, thereby removing Cl and K ions from the CKD.

The leaching and removal efficiency of the Cl and K ions from the CKD was evaluated using X-ray fluorescence (XRF-1800, Shimadzu) after pelletizing with B$_2$O$_3$. The ion content in the leaching solution was then measured by an ion chromatograph (DX-500, Dionex). Scanning electron microscopy (MIRA3, Tescan) and energy dispersive spectroscopy (Bruker, XFlash 6130) were used to analyze the morphology and impurities of the ion-exchange resins surface.
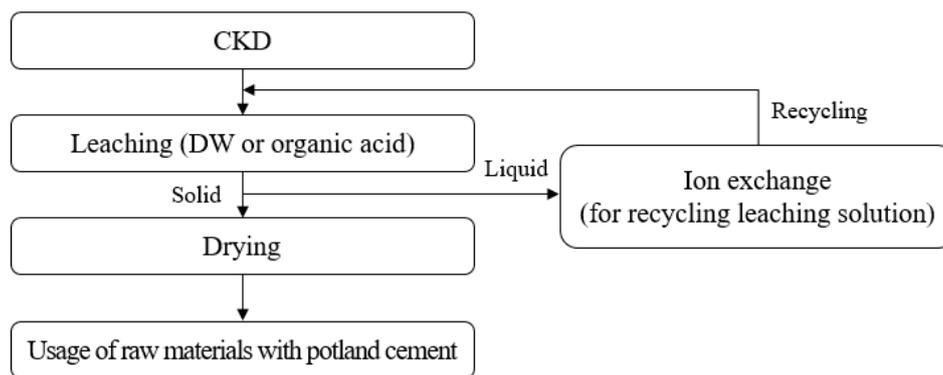
Figure 1. Flow diagram for the leaching and ion-exchange process of cement kiln dust.

Table 2. Properties of CKD powder from SAMPYO cement in South Korea.

Element	CKD (wt%)
Cl	39.10
K	17.85
Ca	18.38
Si	12.62
S	3.51
Al	2.95
Fe	2.76
LoI *	2.83

* Loss on Ignition (105 °C).

3. Results and Discussion

The removal efficiencies of Cl and K were ~87% and ~80%, under 0.5M formic acid. The removal efficiencies were highest for formic acid, followed by oxalic acid, citric acid, and DW; the reaction time varied little between the solutions (Figure 2). As shown in Figure 2, the leaching reaction occurred quickly and it can be seen that the leaching rate was not increased any longer even though the reaction time increased. Suzuki et al. [14] reported that the salt produced, indicated by K_2O, could be recovered by more than 53% by applying NaCl solution. In this study, however, potassium was able to remove more than 80% in 5 min. Similar results have been found in other studies on organic acid leaching for the purpose of waste recycling [15,16]. Musariri et al. [15] reported that citric acid and malic acid both produced a leaching rate of about 70% within 10 min in a cobalt leaching experiment. In this study, the leaching rate did not increase significantly over time.
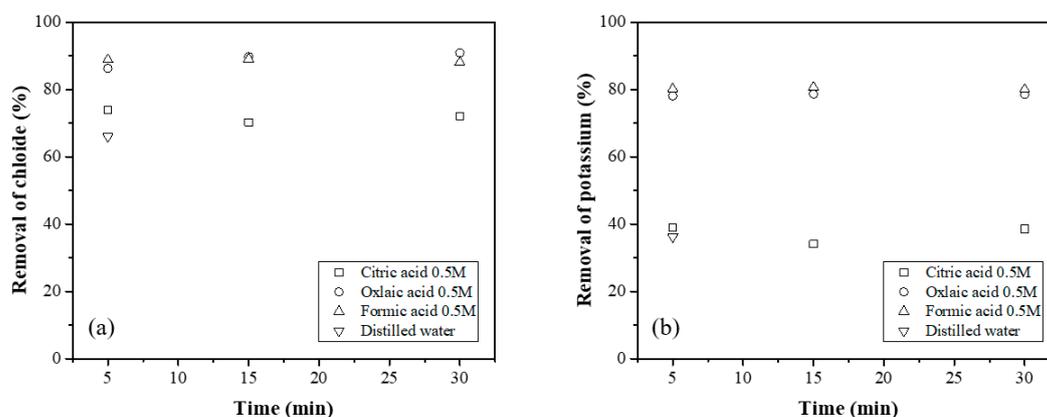
Figure 2. Ion removal efficiency of CKD as a function of the leaching solution; (**a**) chloride and (**b**) potassium. Reaction conditions: L/S (Liquid solid ratio) = 10, 25 °C. 1 atm.

To optimize the safety of CKD recycling, it is important to use solvents that are easy to handle and with minimal environmental concerns. Of the leaching solutions used in this study, DW is the easiest to handle, so its ion removal efficiency was further evaluated by reducing the CKD injection amount to 5 wt% (Figure 3). The removal efficiencies of Cl and K were ~90% and ~83%, respectively, for 1 min of extraction and were similar for up to 5 min of extraction, after which the remaining Ca content was analyzed. The leaching rate increased to 85% for up to 5 min, but Ca began to dissolve in the leaching solution at longer reaction times. This clearly indicates that the extraction reaction time is an important parameter, with an optimal value of ≤5 min in a fixed-bed column. Golpayegani et al. [17] also reported that the chloride or potassium leaching time was an important parameter in an experimental model considering stirring rate, concentration, and temperature.
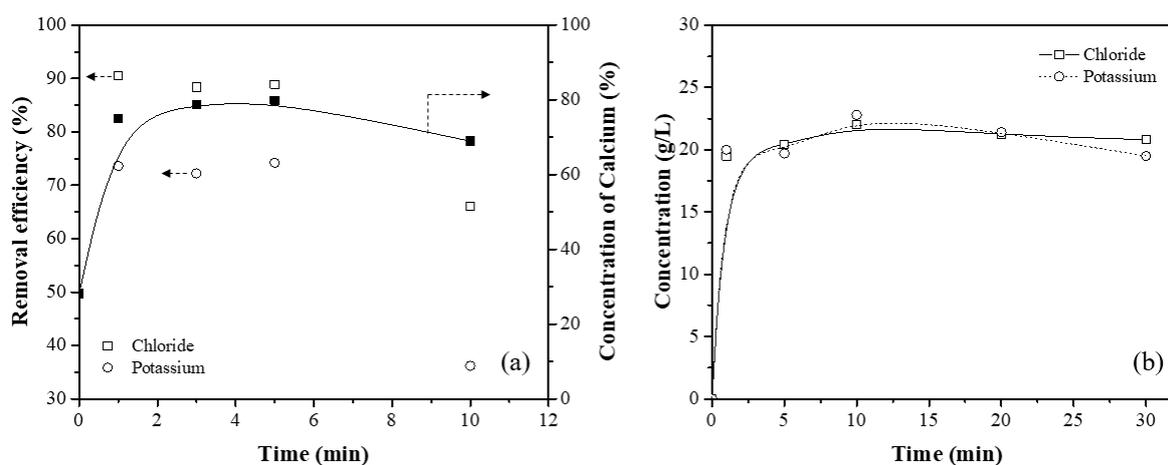
Figure 3. Ion removal efficiency of CKD with distilled water (DW) as a function of the reaction time; (**a**) removal of Cl, K, and concentration of Ca, (**b**) concentration of Cl and K including leached solution. Reaction conditions: L/S = 20, 25 °C. 1 atm.

The ion-exchange capacity was higher at lower flow rates; at 20, 40, and 80 mL/min, the removal rate of Cl ions was ≥99%, 97%, and 70%, and that of K ions was ≥99%, 97%, and 80%, respectively (Figure 4). Liu et al. [18] reported an 80% removal efficiency using the anion-exchange method for the removal of chlorine ions from zinc-production wastewater, meeting the legal requirements for wastewater recycling. Methods for Cl ion removal include chemical precipitation, flocculation, solvent extraction, membrane separation, and ion exchange. The latter has many advantages, including high reaction time, simplicity, and low construction/operation cost [18]. In this study, the Cl and K eluted from CKD was removed easily and effectively via ion-exchange resin, and the optimal operation speed with a fixed-bed column was 40 ml/min. The potential treatment capacity was 267 g-K/L-resin and 255 g-Cl/L-resin, respectively.
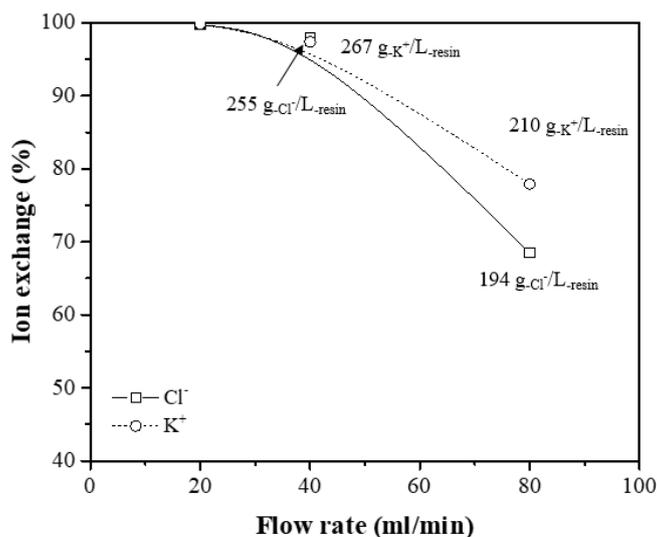
Figure 4. Ion removal efficiency for recycling of spent leaching solution.

SEM analysis of the resin before and after ion exchange showed that cation-resin size ranged from 100 to 700 μm and anion-resin size ranged from 500 to 800 μm (Figure 5). After the reaction, the ion-exchange resin had a rougher surface than before, and surface analysis using energy dispersive spectroscopy (EDS) showed that fresh and spent resin had different components. After the ion exchange, the resin surface contained 12.9% K and 13.5% Cl and the ions in the solution were effectively removed (Figure 4).
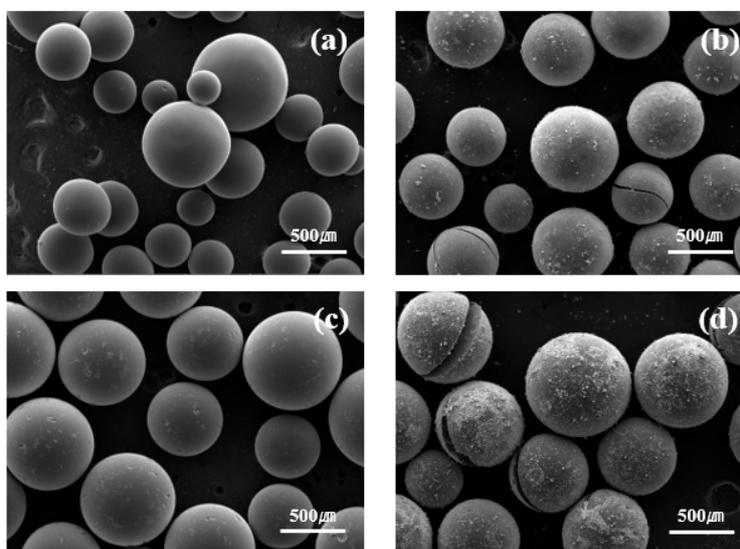
		N	O	S	Al	Si	K	Ca	Fe
Cation resin (%)	**(a) Fresh**	27.2	37.9	34.8	-	-	-	-	-
	(b) Spent	-	42.6	20.2	3.0	2.5	12.9	13.3	5.5

		N	O	F	Cl	Ca
Anion resin (%)	**(c) Fresh**	67.7	28.8	3.6	-	-
	(d) Spent	84.7	-	-	13.5	1.8

Figure 5. SEM images and EDS analysis of ion-exchange resins; (**a**) fresh cation-resin, (**b**) spent cation-resin, (**c**) fresh anion-resin, (**d**) spent anion-resin.

After leaching, the K and Cl ions in the solution were removed by ion exchange, while the leaching solution was recovered and reused up to three times (Figure 6). The removal efficiencies of K and Cl extracted from the CKD were found to be similar, indicating that leaching solution can be effectively recycled. Recycling the leaching solution can significantly reduce the wastewater generated from the CKD treatment, which can have a positive effect on the process operation.
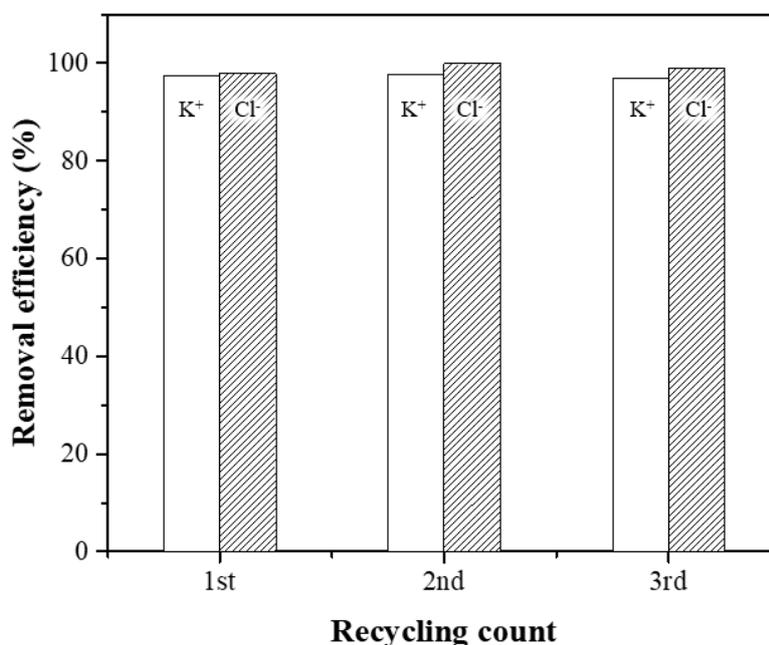
Figure 6. Leaching test of CKD with recycled leaching solution. Reaction conditions: Reaction conditions: L/S = 20, 25 °C. 1 atm.

4. Conclusions

This study assessed the use of different leaching solutions for removing chloride and potassium from CKD to allow its reuse in cement manufacturing. Although organic acids were twice as effective as distilled water, the latter was selected for further tests due to its higher handling safety and ease of recycling. Distilled water was able to remove over 90% of Cl and over 70% of K within 1 min under the condition of L/S 20. In the leaching reaction, the Ca concentration in the CKD increased up to 5 min, however, Ca was eluted at >5 min, reducing the Ca content in the CKD. It was confirmed that control of the reaction time is an important parameter.

Furthermore, Cl and K could be removed from the leachate through ion exchange to allow leaching solution recycling and to minimize wastewater generation. The ion-exchange capacity was 255 g-Cl/L-resin and 267 g-K/L-resin under a flow rate of 40 mL/min, and all showed similar removal efficiencies of 95% or more when recycled and eluted three times after ion exchange.

Author Contributions: Conceptualization, M.S. and S.-S.C.; methodology, M.S. and S.-Y.L. and C.L.; formal analysis, M.S., C.L. and S.-Y.L.; writing—original draft preparation, M.S.; writing—review and editing, M.S. and S.-S.C.; project administration, S.-S.C.

References

1. Edwards, P. Global cement top 100 report 2017–2018. *Global Cement Magazine*, 4 December 2017; 12–20.
2. Coppola, L.; Coffetti, D.; Crotti, E. Plain and ultrafine fly ashes mortars for environmentally friendly construction materials. *Sustainability* **2018**, *10*, 874. [CrossRef]
3. Schorcht, F.; Kourti, I.; Scalet, B.M.; Roudier, S.; Sancho, L.D. *Best Available Techniques (BAT) Reference Document for the Production of Cement, Lime and Magnesium Oxide*; JRC Reference Reports; Publications Office of the European Union: Luxembourg, 9 April 2013; Available online: http://eippcb.jrc.ec.europa.eu/reference/BREF/CLM_Published_def.pdf (accessed on 16 September 2019).
4. Sreekrishnavilasam, A.; King, S.; Santagata, M. Characterization of fresh and landfilled cement kiln dust for reuse in construction applications. *Eng. Geol.* **2006**, *85*, 165–173. [CrossRef]
5. Kunal; Siddique, R.; Rajor, A. Use of cement kiln dust in cement concrete and its leachate characteristics. *Resour. Conserv. Recycl.* **2012**, *61*, 59–68. [CrossRef]
6. Maslehuddin, M.; Al-Amoudi, O.S.B.; Shameema, M.; Rehmana, M.K.; Ibrahim, M. Usage of cement kiln dust in cement products—Research review and preliminary investigations. *Constr. Build. Mater.* **2008**, *22*, 2369–2375. [CrossRef]
7. Miller, G.A.; Zaman, M. Field and laboratory evaluation of cement kiln dust as a soil stabilizer. *Transp. Res. Rec.* **2000**, *1714*, 25–32. [CrossRef]
8. Siddique, R. Utilization of Cement Kiln Dust (CKD) in cement mortar and concrete-an overview. *Resour. Conserv. Recycl.* **2006**, *48*, 315–338. [CrossRef]
9. Lanzerstorfer, C. Residue from the chloride bypass de-dusting of cement kilns: Reduction of the chloride content by air classification for improved utilisation. *Process Saf. Environ. Prot.* **2016**, *104*, 444–450. [CrossRef]
10. Tennis, P.; Bhatty, J.I. Characteristics of portland and blended cements: Results of a survey of manufacturers. In Proceedings of the IEEE Cement Industry Technical Conference, Phoenix, AZ, USA, 9–14 April 2006; pp. 83–101. [CrossRef]
11. Al-Harthy, A.S.; Taha, R.; Al-Maamary, F. Effect of cement kiln dust (CKD) on mortar and concrete mixtures. *Constr. Build. Mater.* **2003**, *17*, 353–360. [CrossRef]
12. Aidan, C.; Trevor, C. Cement kiln dust. *Concrete* **1995**, *29*, 40–42.
13. El-Attar, M.M.; Sadek, D.M.; Salah, A.M. Recycling of high volumes of cement kiln dust in bricks industry. *J. Clean. Prod.* **2017**, *143*, 506–515. [CrossRef]
14. Suzuki, T.; Saunders, J.; Tamura, N.; Saito, S. Recovering Potassium Salt for Fertilizer Use from Chlorine Bypass Dust. *Taiheiyo Cement Kenkyu Hokoku* **2012**, *162*, 37–42.
15. Musariri, B.; Akdogan, G.; Dorfling, C.; Bradshaw, S. Evaluating organic acids as alternative leaching reagents for metal recovery from lithium ion batteries. *Miner. Eng.* **2019**, *137*, 108–117. [CrossRef]
16. Halli, P.; Hamuyuni, J.; Leikola, M.; Lundstron, M. Developing a sustainable solution for recycling electric arc furnace dust via organic acid leaching. *Miner. Eng.* **2019**, *124*, 1–9. [CrossRef]
17. Golpayegani, M.H.; Abdollahzadeh, A.A. Optimization of operating parameters and kinetics for chloride leaching of lead from melting furnace slag. *Trans. Nonferr. Met. Soc. China* **2017**, *27*, 2704–2714. [CrossRef]
18. Liu, W.; Lu, L.; Lu, Y.; Hu, X.; Liang, B. Removal of chloride from simulated acidic wastewater in the zinc production. *Chin. J. Chem. Eng.* **2019**, *27*, 1037–1043. [CrossRef]