



Manufacture of potassium chloride from cement kiln bypass dust: An industrial implementation case for transforming waste into valuable resources

Jiajun Wang^{a,b,c}, Pu Zeng^{b,c}, Zhe Liu^{b,c}, Yeqing Li^{a,c,*}

^a College of Materials Science & Engineering, Wuhan University of Technology, 122 Luoshi Road, Wuhan, 430070, China

^b Huaxin Environmental Engineering Co., Ltd., No. 426, Gaoxin Avenue, Wuhan, 430073, China

^c Huaxin Cement Co., Ltd., No. 426, Gaoxin Avenue, Wuhan, 430073, China

ARTICLE INFO

Keywords:

Cement kiln collaborative disposal
Domestic waste
Bypass dust
Potassium salt
Carbon reduction
Resource utilization
Sustainability

ABSTRACT

The recirculation of chlorine within the kiln presents a major hurdle in co-processing domestic waste in cement kilns. This chlorine enrichment not only adversely affects the quality of cement, but also pose a serious challenge to the subsequent eco-friendly disposal of kiln dust. To solve this problem, a proper bypass system has been implemented in this study on a 4000 t/d new dry process cement rotary kiln, and the collection of chlorine-rich bypass dust outside the kiln (30 t/d) has been achieved. In addition, a comprehensive and innovative system has been developed, including water washing and subsequent triple-effect salt extraction, to achieve leaching of K^+ and Cl from the bypass dust in the water rinsing liquid, while effectively removing harmful metal ions such as Pb^{2+} . Finally, the extraction of high-purity KCl salt (6 tons/day, purity of 90 %) has been successfully achieved. It is worth noting that high-temperature flue gas rich in CO_2 has been used to precipitate certain heavy metal ions, while steam from the waste-heat power generation system has been employed as a heat source for the potassium salt evaporation process. More importantly, all the materials, except for the KCl salt product, are returned to the cement kiln system without causing any secondary pollution. This study not only effectively addresses the negative impacts of chlorine element circulation within cement kilns during domestic waste co-processing, but also achieves a highly innovative engineering practice of transforming waste into valuable resources from kiln dust to high-purity KCl products. In brief, this work provides a reference example for future approaches to clean production, carbon reduction and resource utilization in the cement industry.

1. Introduction

Cement is an indispensable and extensively employed building material globally and has an important impact on urbanization and sustainable economic and social development in all countries [1]. However, cement production inevitably consumes a lot of energy and produces high amounts of CO_2 emissions [2]. To achieve carbon reduction goals and environmental sustainability, the cement industry is striving towards technological innovations such as low-carbon products, collaborative disposal, alternative fuels and raw

* Huaxin Cement Co., Ltd., No. 426, Gaoxin Avenue, Wuhan, 430073, China

E-mail addresses: wangjiajun@huaxincem.com (J. Wang), zengpu@huaxincem.com (P. Zeng), liuzhe@huaxincem.com (Z. Liu), liyeqing@huaxincem.com (Y. Li).

<https://doi.org/10.1016/j.heliyon.2023.e21806>

Received 8 August 2023; Received in revised form 8 October 2023; Accepted 29 October 2023

Available online 7 November 2023

2405-8440/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

materials (AFR), and carbon capture and utilization on [3,4].

The use of 100 % alternative fuels and raw materials (AFR) (i.e. zero fossil fuels) is a desirable goal for the future cement industry [4,5]. Currently, cement kiln collaborative disposal of domestic waste is an important way to approach this goal [4,6]. However, the average chlorine content of these domestic wastes in China is about 0.2–0.5 wt % [7]. As the AFR materials are exposed to the kiln's high temperature atmosphere, repeated volatilization and condensation of Cl element can cause the accumulation of Cl-rich dust within the kiln [8,9]. This issue will not only result in crusting and clogging in the tail chamber, decomposer and preheater, but also significantly affects the quality of cement clinkers [10].

The cement kiln bypass process is a well-known and effective method of breaking the internal recirculation of the chlorine element in kiln systems [11,12]. The strategy of the process is to install a bypass device on the front or rear side of the kiln tail chamber to extract a certain percentage (~5 %) of the high-temperature flue gas out of the kiln [11]. In this process, volatile and harmful elements (such as chlorine, sulfur, alkali, etc.) in the kiln are separated from the kiln system along with the flue gas and are collected in the bypass dust after air cooling, filtration, and dust collection treatment. As a consequence, the issue of Cl recirculation in the kiln is resolved, but a large amount of bypass dust is emitted after the bypass process. However, improper disposal of bypass dust with high chlorine content will cause serious environmental problems. It is also worth noting that chlorine-alkali-rich bypass dust is undoubtedly a useful solid waste resource. Therefore, there is an urgent need to explore feasible ways for harmless disposal and efficient resource utilization of the chlorine-rich bypass, which is of great significance for the carbon reduction and circular economy of the cement industry.

For decades, considerable efforts have been devoted to the environmentally-safe disposal and effective resource utilization of bypass dust [12–17]. Currently, the bypass dust is typically used as a blending material for cement or mortar in the production of hollow blocks, cement masonry, plastering mortar, and pavement bricks [14,15]. Another promising utilization route for chlorine-rich bypass dust is the extraction and separation of chloride-salts or potassium salts from the dust, which has significant environmental and economic benefits for the cement industry. Daous et al. [16] extracted potassium salts from the alkali-rich cement kiln dust (CKD) of a Saudi Arabia cement factory. However, the study did not provide any information on the exact chemical composition and purity of the potassium salts. Kim et al. [17] obtained a solution enriched with potassium chloride by washing the bypass dust, which unfortunately was not subsequently treated. The solution could not be used directly as a potash fertilizer nutrient solution due to its high pH value of 10.65. In general, the above resource utilization and treatment methods for the chlorine-rich bypass dust are still in the exploratory or small-scale trial stage. Therefore, there is a significant need for mature, large-scale and cost-effective disposal technologies. In addition, concerns regarding salt purification and heavy metal contamination during salt extraction from bypass dust must be considered. Furthermore, it is imperative to fully utilize the technical conditions of cement production, including waste heat, exhaust gases, and liquid/gas filtration systems, to ensure the low cost and sustainability of the bypass dust disposal process.

To address the above issues, the migration of chlorine from the AFR to the bypass dust has been tracked via elemental and phase analysis in this study. The enrichment of chlorine and potassium elements and the high potassium/sodium ratio in the bypass dust have been determined. In addition, we have taken full advantage of the technological conditions of cement production to develop a complete set of industrial-scale treatment processes and devices for water washing, and salt extraction of the chlorine-rich bypass dust. In terms of technological innovations, high-temperature flue gas rich in CO₂ has been used to precipitate certain heavy metal ions, while steam from the waste-heat power generation system has been employed as a heat source for the potassium salt evaporation process. Furthermore, the problem of separating KCl salt and NaCl salt, as well as reducing the content of residual heavy metals in the salt, is effectively solved through the implementation of the three-effect evaporation system and cooling crystallization technology of KCl at a predetermined temperature. Although we employed established physical and chemical reactions, along with mature industrial technologies, we have successfully developed a novel industrial production line capable of consistently extracting high purity KCl salt (purity >90 %; >6 t/d) from the bypass dust.

It is worth noting that potassium salts are of great importance for the development of Chinese agriculture. A less well-known fact is that 56 % of China's arable land is deficient in potassium, and most of the world (except for Canada, Russia, and Belarus) is also dependent on imported potash salts. Thus, the production of potassium chloride from cement kiln bypass dust in this study achieves both harmless and resourceful disposal of chlorine-containing kiln dust and is significant in addressing the shortage of potash fertilizer for arable land in China.

2. Processes and methods

2.1. Introduction of the cement kiln in this study

In this study, experiments were carried out on a 4000 t/d new suspension (NSP) production line with a five-stage preheater at a plant of Huaxin Cement Co., Ltd. Domestic waste, municipal sludge, general solid waste, and other wastes were used as alternative fuels and raw materials (AFR) in this kiln. The kiln's disposal capacity was set at 500 tons/day for domestic waste, 600 tons/day for municipal sludge and 500 tons/day for general solid waste, respectively.

2.2. Bypass ventilation facility and bypass dust collection system

To break the cyclic accumulation of chlorine in the kiln, a kiln line with a bypass system was designed and installed. The workflow of the bypass system was illustrated in Fig. 1.

As shown in Fig. 1, the system basically consists of a set of gas induced draft fans, a cooling fan, a cyclone separator (for coarse particle separation), a bag dust collection (for fine particle separation), and a bypass dust bin. In operation, approximately 10 vol% of the flue gas was extracted from the kiln tail chamber and mixed with air from the cooling fan to cool the flue gas rapidly. The cooled dusty gases were collected as dust after passing through a cyclone separator and a bag filter. Those coarse particles separated by the cyclone were fed into the dust bin and finally reintroduced into the kiln system. The fine particles collected by the baghouse were fed into a second bypass dust bin and eventually into the dust handling system as the bypass dust.

2.3. Kiln dust water-washing and salt-extraction facilities

In this study, a complete process for bypass dust washing (120 t/day) combined with salt extraction from the leaching solution was developed. The system was designed to consist of a washing tank, slurry pump, vacuum drum filter, shallow aeration tank, dosing device, inclined plate sedimentation tank, triple effect evaporation salt-making system, supporting pumps, condensate tank, and cake conveyor belt. The process flow of KCl extraction using bypass dust as raw materials was shown in Fig. 2.

Specifically, the bypass dust from the dust silo was poured into a washing tank with a water/dust weight ratio greater than 3:1, maintaining sufficient agitation to dissolve the soluble chloride salts in the water as much as possible. The slurry was subsequently pumped into a solid-liquid separator for solid-liquid separation. The filtrate was fed into a salt extraction system, while the separated solid waste with a moisture content of less than 30 % and almost no chlorine was reintroduced back into the kiln for utilization.

As noted, the solid content of the filtrate was controlled at 0.05 %. The filtrate was sent to a calcium-removal tank, aerated by the tail gas rich in CO₂ from the cement kiln. Calcium ions in the water were combined with CO₂ to form insoluble CaCO₃ precipitates, which were sent to a sedimentation tank for removal, while the supernatant from the sedimentation tank was sent to a brine tank for salt extraction. Most of the heavy metal ions in the supernatant were removed by adding chemical agents, and then the supernatant entered a reverse triple-effect salt evaporation system after the impurities were removed using a cartridge filter.

In the three-effect evaporation system, hot steam was provided by the cement kiln waste heat power generation system, and the industrial KCl crystalline salt products were separated through a temperature control system. Notably, the condensate from the salt extraction process was returned to the system for the water washing process, while a small amount of the mother liquor remaining after thermal evaporation was reintroduced into the kiln to be used as fuel. Moreover, the entire system was enclosed, only the potassium chloride product was output, and no other secondary pollutants were generated. In addition, the tail gas and steam of the cement kiln were fully utilized, reducing production costs. Therefore, the production process was very clean.

2.4. Characterizations and testing methods

The mineral phase composition of the bypass dust and crystallized salts was determined by an X-ray diffractometer (XRD) (Bruker D4, Germany), using a CuK_α radiation source at a tube voltage of 40 kV and a tube current of 40 mA over a 2-theta range of 8°–65° with

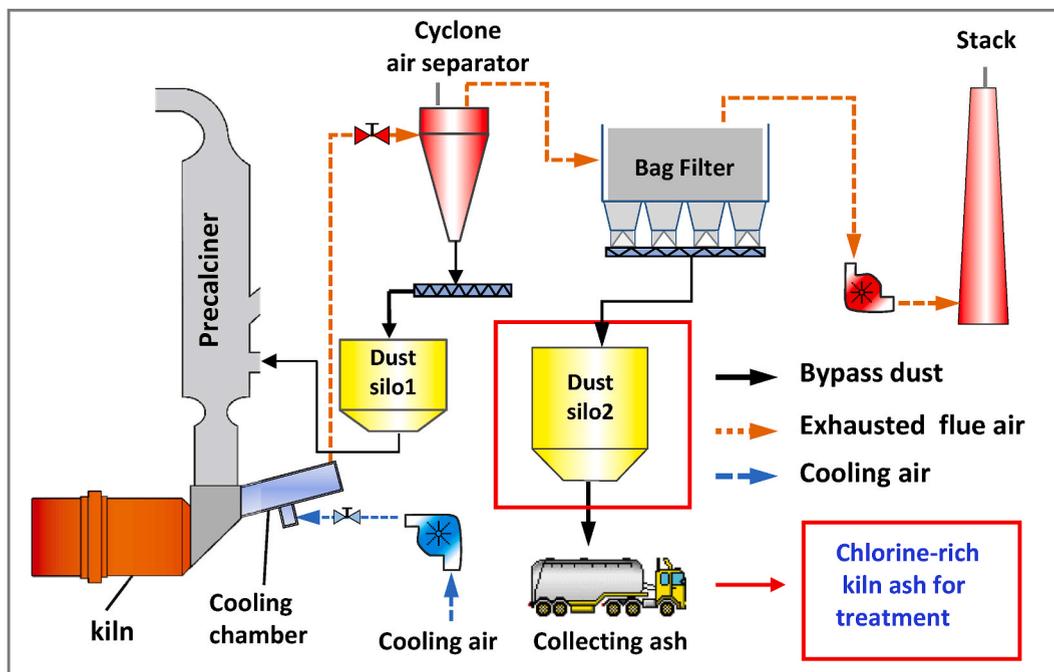


Fig. 1. Illustration of the cement kiln bypass system.

produced without using the bypass system, clinker samples produced using the bypass exhaust system, and bypass dust samples collected in the bypass collection system.

The results calculated in the form of elemental oxides are presented in Table 1. The content of chlorine element in the raw materials sample is $\sim 0.02\%$, and the content of chlorine element introduced in the AFR sample is $\sim 0.35\%$. Note that chlorine can be easily circulated and enriched in the kiln system (rotary kiln and preheater), and it is also easy to cause a significant increase in the chlorine content in the clinker. The table also confirms that the clinker samples produced without using a bypass system contained up to 0.12% chlorine. In contrast, the chlorine content of the hot raw materials is 3.23% , while that of the clinker samples is significantly reduced to 0.034% , which fully meets the quality requirements for clinker production. The contents of Cl and K in the bypass dust exceed 10% , indicating that the bypass process effectively enriches chlor-alkali elements in the dust, leading to a significant decrease in chlorine content in the clinker.

To visually compare the K/Na content ratio in different samples, the corresponding results are shown in Fig. 3 in the form of a histogram. As shown, the proportions of the K and Na elements in the kiln raw materials are relatively low, with the total content being less than 1.0% . The K_2O content is $\sim 0.38\%$, Na_2O content is $\sim 0.12\%$, and K/Na content ratio is 3.54. The contents of K_2O and Na_2O in the clinker increase slightly (0.56% and 0.26% , respectively). The K/Na content ratio is 2.41, lower than that of the raw materials (3.54). This result verifies that K is more volatile than Na in the kiln, and thus, the volatile K mainly combines with the Cl element in the kiln to form KCl compounds. This can be attributed to the fact that the thermodynamic drive to form KCl is greater than that of NaCl. Note that the K content calculated using K_2O increases significantly in the hot raw materials samples (3.71%), cyclone bypass dust (4.45%), and dust bag bypass dust (14.41%), respectively. The contents of Na_2O in the corresponding samples are 0.81% , 0.82% , and 1.01% , respectively, with a slight increase. The corresponding K/Na content ratio is significantly higher than that in the hot raw materials (5.12), cyclone bypass dust (6.07), and dust bag bypass dust (15.96) samples. The results indicate that the concentration of K in the bypass dust is pronounced, with a certain degree of Na enrichment. The K and Na contents in the bypass dust are approximately 44 and 8.4 times those of the raw materials, respectively.

To clarify the migration process of K and Cl elements from the raw materials and fuels to the bypass dust, XRD phase analyses were carried out on the kiln's raw materials, hot raw materials, cyclone dust, and dust collector dust (bypass dust) from the same batch, as shown in Fig. 4. The relative content of each crystalline phase was quantitatively analyzed and estimated using the Jade software. Note that the samples inevitably contain uncrystallized or amorphous phases, and the Ratio of Intensity Reference (RIR) values supplied by Jade are often imprecise. Therefore, the content estimated from the XRD spectra is only a semi-quantitative analysis, which can only be used for comparative analysis of the differences between the phases of different samples, but not for quantitative analysis. As shown in Fig. 4(a), the main mineral components of the kiln raw materials are $CaCO_3$ ($\sim 90.2\text{ wt}\%$), SiO_2 ($\sim 7\text{ wt}\%$), and Muscovite phase ($\sim 2.8\text{ wt}\%$), wherein the Muscovite phase contains about $11\text{ wt}\%$ of K_2O and a very low amount Na. The content of K element in the raw materials is $\sim 0.30\%$. As shown in Fig. 4 (b), the cooled hot raw materials mainly contain CaO, SiO_2 , C_2S , $CaCO_3$, and KCl phases, wherein the content of KCl is approximately 8.6% , which is converted into the K element content of $\sim 4.5\text{ wt}\%$. Generally, the mass of the hot raw materials is about 71% of the raw materials. If all of the K element in the raw materials goes into the hot raw materials, its content in the hot raw materials can reach about 0.42% . However, the actual K content present in the hot raw materials is approximately 10–20 times of the K element content in the raw materials. In addition, the raw materials exhibit a significantly low chlorine content. is very low. Therefore, the enrichment of KCl in the hot raw materials does not inherent to the raw materials, but rather, is primarily a result of the volatilization and combination of K^+ from the raw materials and the Cl^- introduction from the AFR during the high-temperature zone. This is consistent with previous predictions that KCl compounds could be formed in cement kilns [9]. The KCl compound then absorbed on the surface of the hot raw materials with hot air flow. As depicted in Fig. 4 (c), the KCl crystallization diffraction peaks in cyclone kiln dust exhibit high sharpness, and the estimated a corresponding content is approximately 21.9% . Fig. 4

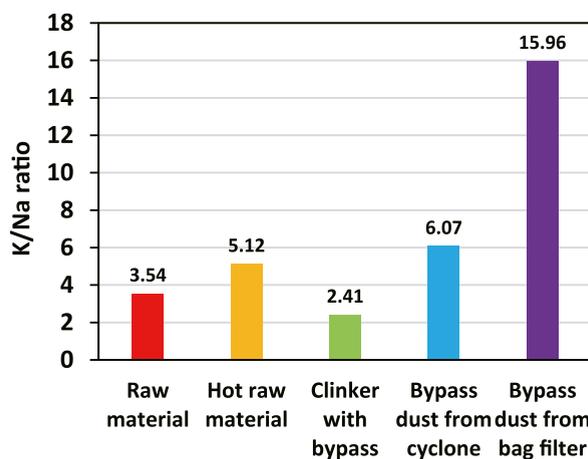


Fig. 3. Comparison of K/Na content ratio for different samples.

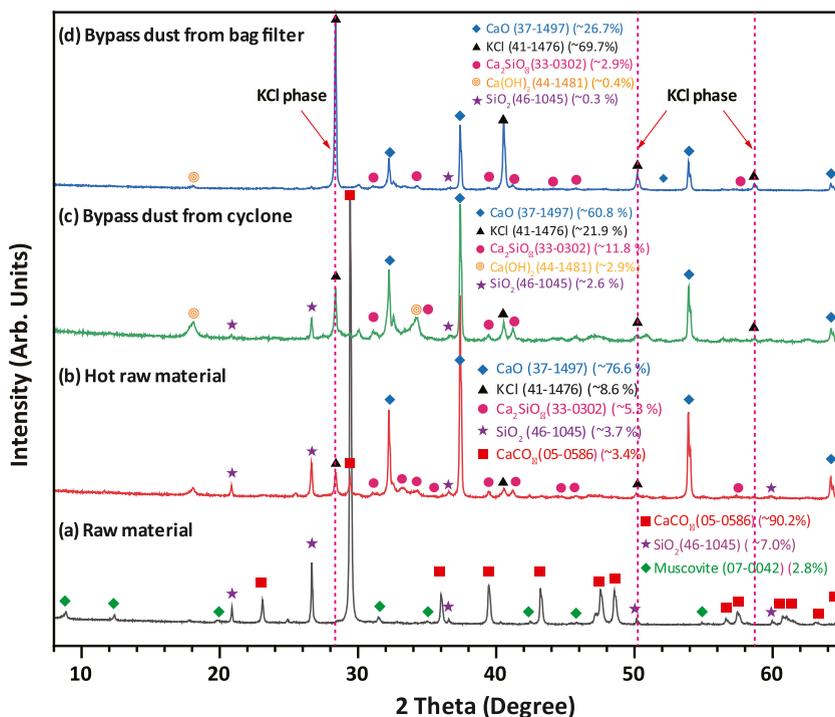


Fig. 4. Comparison of X-ray diffraction (XRD) patterns of different samples.

(d) portrays the XRD pattern of the bypass dust obtained from the dust collection bag. The main crystalline phases of the bypass dust include KCl, CaO, C₂S, Ca(OH)₂, and SiO₂, among which the content of KCl is the highest (69.7 wt%). The XRD results indicate that the Cl and K elements are enriched in the bypass dust in the form of KCl, wherein the K element is mainly introduced in the kiln by raw materials, and the Cl element is introduced by the AFR and the raw materials. The high-temperature atmosphere in the kiln and the strong volatility and easy combination of K and Cl elements results in the formation and circulation of KCl in the kiln. Moreover, the

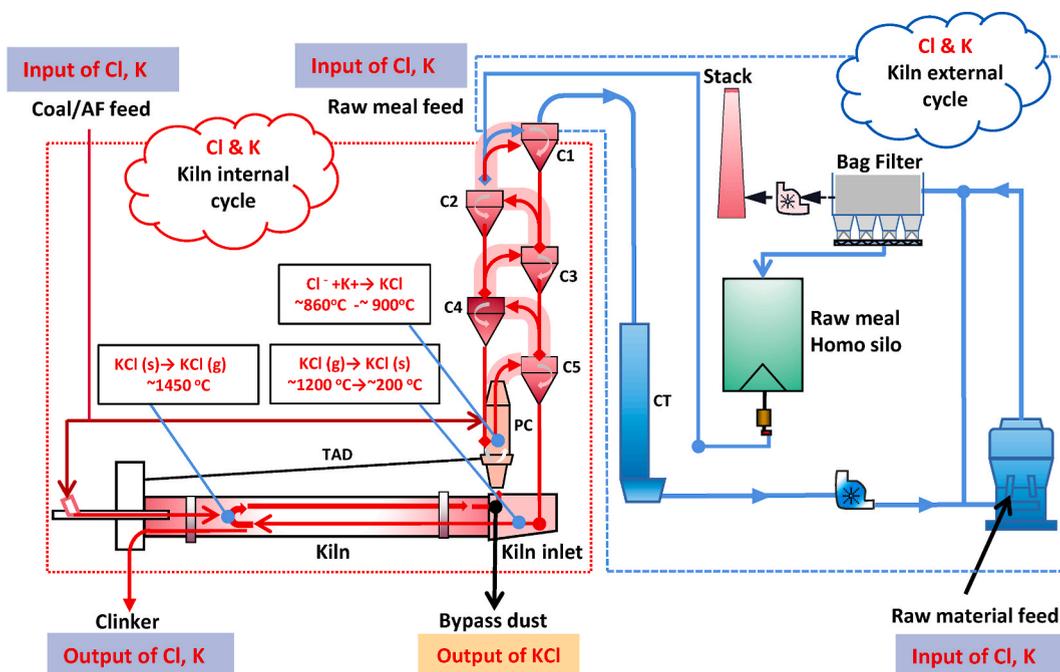


Fig. 5. Schematic diagram of the recirculation and migration of Cl and K elements in a cement kiln system.

bypass ventilation enables the enrichment of KCl in the bypass dust and offers the possibility to recover KCl outside the kiln. As reported, Han et al. [18] analyzed bypass dust samples from a cement plant in Korea and found the KCl content in the bypass dust as high as 19.46 %. Uliasz-bocheńczyk [19] demonstrated that the contents of K and Cl in the bypass dust were significantly higher than those in the kiln dust, and the KCl content in the bypass dust was about 10 %. The results reported in the literature are consistent with the results of this study. combined with the elemental analyses shown in Tables 1 and it can be seen that the bypass dust contains a small amount of NaCl in addition to the major KCl. Since the physicochemical properties of NaCl and KCl are similar, the formation and enrichment mechanism of NaCl is presumed to be the same as that of KCl. However, owing to the low content of the crystalline phase of NaCl (<5 wt %), the corresponding characteristic diffraction peaks are hard to observe in the XRD patterns.

The migration processes of Cl, Na, and K elements in the kiln system based on the above results and analysis are illustrated in Fig. 5. As shown, the K and Na elements are introduced into the cement kiln system from the raw materials, while the Cl elements are mainly brought into the system by the ARF. In general, these elements are strongly enriched in cement kilns due to their high volatility and reactive combinatorial properties in the high-temperature environment of the kilns. The bypass process can effectively break the recirculation of the K, Na, Cl, and other elements in the kiln and finally realize the enrichment of chloride-alkali elements in the bypass dust. The chloride-alkali elements mainly exist in the form of KCl crystalline compounds, along with a small amount of NaCl.

3.2. Analysis of the water-washing and salt-extraction process of the bypass dust

The above chemical and phase analyses of the bypass dust indicate that the chlorine element in the kiln dust existed in the form of chloride-alkali salts, and the proportion of KCl in the bypass dust has an obvious advantage over NaCl. Due to the high solubility of chloride-alkali salts in water, it is beneficial to extract higher-purity KCl crystals in the subsequent water-washing process of the bypass dust.

The obtained bypass dust was then washed with water at a water/dust weight ratio of 4:1 and a continuous stirring time of 15 min. The slurry was pumped into a solid-liquid separator to obtain a filtrate and the insoluble filter residue. The filtered residue was dried and reintroduced into the kiln. The concentrations of various ions in the washed filtrate samples were tested by a combination of an Inductive Coupled Plasma Emission Spectrometer (ICP) and a titration method, and the results are shown in Table 2.

As seen, the concentration of K^+ in the filtrate after washing is relatively high (28.21 mg/mL), which is beneficial for the subsequent salt-extraction treatment. The concentrations of Cl^- and Na^+ were 24.06 mg/mL and 0.73 mg/mL, respectively. Note that the concentration of Ca^{2+} in the washing solution is relatively high (2.32 mg/mL) as well. The high concentration of Ca^{2+} results in the entire washing solution being strongly alkaline (PH=12.36), which will cause serious corrosion and scaling to the washing and salt-extraction equipment. Therefore, it is important to remove the Ca^{2+} before salt extraction. In addition, the washing solution contained high concentrations of Pb^{2+} (52.4 mg/mL) and Cr^{2+} (0.269 mg/mL). Note that if these components enter the final crystalline salt product, it will definitely cause the content of heavy metals in the potassium salt product to exceed the standard. Therefore, Pb^{2+} and Cr^{2+} must be removed.

In addition, the contents of Cl, S, K, and Na elements in the bypass dust sample and the water-washing solution were compared, and the recovery rates of these elements in the solution were calculated. The results are presented in Table 3. As seen, the extraction rates of Cl, S, K, and Na elements in the bypass dust are 76.62 %, 35.45 %, 68.52 %, and 25.30 %, respectively. The above results indicate that most of the Cl and K elements in the bypass dust are enrichment in the filtrate after washing and separation, which benefits the subsequent extraction of KCl potassium salts.

The filtrate obtained after direct water-washing and solid-liquid separation could not be used for direct salt extraction, and thus, a pretreatment was required. In this study, CO_2 from the flue gas at the end of the kiln was employed to pre-treat the filtrate. Table 2 compares the changes in the pH value and the content of various metal ions in the filtrate before and after pretreatment. It shows that

Table 2

The concentrations of the various ions in water-washing filtrate samples before and after CO_2 pretreatment.

Test items	Unit	Filtrate	Filtrate after CO_2 pretreatment
pH	–	12.36	7.01
K^+	mg/mL	28.21	27.40
Na^+	mg/mL	0.73	0.75
Ca^{2+}	mg/mL	2.32	1.13
Cl^-	mg/mL	24.06	23.85
SO_4^{2-}	mg/mL	7.02	7.14
Hg	mg/L	<0.010	<0.010
As	mg/L	<0.1	<0.1
Cd	mg/L	<0.004	<0.004
Co	mg/L	<0.002	<0.002
Cr	mg/L	0.269	0.253
Cu	mg/L	<0.002	<0.002
Mn	mg/L	<0.002	<0.002
Ni	mg/L	<0.005	<0.005
Pb	mg/L	52.4	0.27
Sb	mg/L	<0.02	<0.02
Zn	mg/L	0.03	<0.02

Table 3

The recovery rate of Cl, S, K, and Na elements from the bypass dust to the washing solution.

	Element in bypass dust (Per 1000 kg)	Element infiltrate (Per 3500 L)	Element recovery rate (R)
Element	C ₀ (%)	C ₁ (g/L)	$R = 10 * C_1 * 3500 / (C_0 * 1000)$ (%)
Cl	10.99	24.06	76.62
S	2.31	2.34	35.45
K	14.41	28.21	68.52
Na	1.01	0.73	25.30

the CO₂ treatment can significantly reduce the PH value of the filtrate and cause metal ions, such as Ca²⁺ and Pb²⁺, to precipitate in the form of carbonate, thus, reducing the content of metal ions in the filtrate. The possible principle for the removal of metal ions by CO₂ pretreatment is speculated as follows.

The chemical reactions involved in the precipitation of Ca²⁺ and Pb²⁺ during the CO₂ pre-treatment may be as shown in Eqs. (1)–(4):



From the equation, it can be seen that in the initial stage of introducing CO₂, the CO₂ reacts with OH⁻ in the filtrate to produce CO₃²⁻, while consuming the OH⁻ in the liquid. At this stage, the pH value of the filtrate begins to decrease significantly until it becomes neutral. However, when excessive CO₂ is introduced into the water, HCO₃⁻ will be further generated, resulting in an increase in the pH value. Specifically, the Ca²⁺ in the filtrate can react with CO₂ to form a CaCO₃ precipitate, thereby gradually reducing its concentration in the filtrate. However, if the amount of CO₂ is excessive, part of the precipitate will be converted into soluble Ca(HCO₃)₂ and enter the filtrate again. Therefore, the amount of CO₂ should be maintained at an appropriate level. In addition, it is worth noting that the order of precipitation of metal carbonates in the solution depends on the competition between the concentration product constant of the precipitate (K_{sp}) and the concentration product of the ions to be precipitated (Q). The ion whose ion product (Q) first exceeds K_{sp} is precipitated first, that is, the smaller the K_{sp} of the precipitate, the more preferentially precipitated. In this study, Pb²⁺ has the highest concentration (52.4 mg/mL), so its ion product is the largest in the CO₃²⁻-ion containing filtrate, while its corresponding insoluble carbonate (PbCO₃) has the smallest K_{sp} (3.3×10^{-14}) among all the metal carbonates, therefore, Pb²⁺ will precipitate before other metal ions. As presented in Table 2, after the CO₂ treatment, the concentration of Pb²⁺ reduces significantly from 52.4 mg/mL to 0.27 mg/mL. Furthermore, this concentration can be subsequently reduced to an environmentally safe level by activated carbon adsorption. As for Zn²⁺, since the K_{sp} (1.44×10^{-10}) of ZnCO₃ is very close to the K_{sp} (8.7×10^{-9}) of CaCO₃, it is easily co-precipitated with CaCO₃ in the form of ZnCO₃, or adsorbed by CaCO₃. As seen in Table 2, after the CO₂ treatment, the concentration of Zn²⁺ reduces from 0.03 mg/mL to <0.02 mg/mL. However, the residual heavy metal element Cr³⁺ (0.269 mg/mL) in the filtrate is hard to remove, because the Cr³⁺ ion is difficult to form a corresponding insoluble precipitate phase in the alkaline filtrate. The concentration of Cr³⁺ decreases slightly (0.253 mg/mL) after the CO₂ treatment as seen in Table 2. Therefore, it is also necessary to reduce this content by subsequent activated carbon adsorption and chemical reduction precipitation. According to Okhrimenko et al. [20], the structure of the CaCO₃ phase precipitated from solution is usually a calcite phase transformed from an amorphous form. Moreover, the precipitated

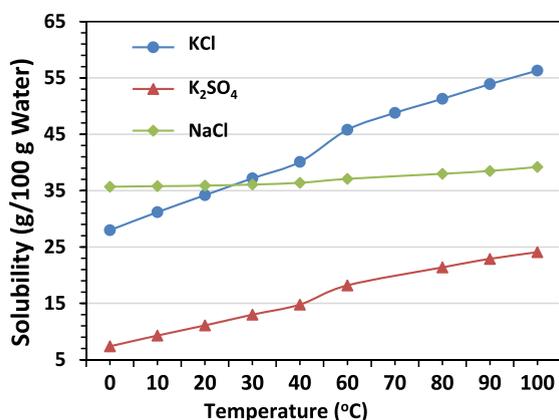


Fig. 6. Solubility curves of KCl, NaCl, and K₂SO₄ in the temperature range of 0–100 °C. (Note that the solubility data for every temperature used to plot this figure comes from CRC Handbook of Chemistry and Physics [21]).

CaCO_3 phase has a chelating effect on a variety of toxic divalent metal ions in the filtrate due to its high specific surface area and mesoporous structure. Thus, the mechanism of CO_2 pretreatment of filtrate can be summarized as the precipitation reaction of CO_2 with metal ions and the chelating and adsorption of the generated CaCO_3 phase. In short, results demonstrate that the reduction of the pH value of the filtrate can be finally realized by CO_2 pretreatment, and most of the undesired metal ions such as Ca^{2+} and Pb^{2+} have been removed while the desired K^+ and Cl^- are retained. Undoubtedly, this pretreatment greatly saves the cost of employing chemicals to remove all unwanted impurities from the filtrate.

After CO_2 pretreatment, the pretreated filtrate is then passed through a sedimentation tank followed by a safety filter to remove the residual unwanted chemical impurities. Finally, the clarified filtrate is introduced into a three-effect evaporation system for salt extraction. In this stage, the main cations in the filtrate are K^+ and Na^+ , while the main anions are Cl^- and SO_4^{2-} . It is clear that these ions in the filtrate can be precipitated in the form of three main salts, namely KCl, NaCl, and K_2SO_4 . Therefore, to extract pure KCl, it is necessary to develop a suitable extraction process based on the solubility of the three salts and the difference in their solubility at elevated temperatures. Based on the previously reported solubility data [21], the solubility values corresponding to NaCl, KCl, and K_2SO_4 in the temperature range of 0–100 °C are plotted in Fig. 6. As shown, the solubility of KCl varies greatly from 20 °C to 100 °C (from 34.2 g/100 g water to 56.3 g/100 g water). The solubility of K_2SO_4 also changes significantly (from 11.1 g/100 g water to 24.1 g/100 g water), while that of NaCl is almost constant with temperature (35.9–39.2 g/100 g water). From the above solubility characteristics, it can be seen that in the temperature range of 0–100 °C, the solubility of K_2SO_4 in water is the smallest, and that of KCl is the largest. Therefore, during cooling crystallization, K_2SO_4 will crystallize and precipitate first, followed by KCl and NaCl. In addition, although the solubility of NaCl is lower than that of KCl, it cannot precipitate easily compared to KCl. This is because the Na^+ content in the filtrate is as low as 3 % of the corresponding K^+ content, that is, the concentration of the sodium salt during thermal evaporation is much lower than its saturation solubility.

Based on the above analysis, we have established a reasonable three-effect evaporation process, in which the filtrate enters from the third effect, the hot steam provided by the waste heat power generation system of the cement kiln enters from the first effect, so that the flow direction of the filtrate and steam is opposite. In this system, the filtrate is passed through a third-effect heating separator and a second-effect heating separator successively. When the temperature of the second-effect separator is stabilized at the set boiling point,

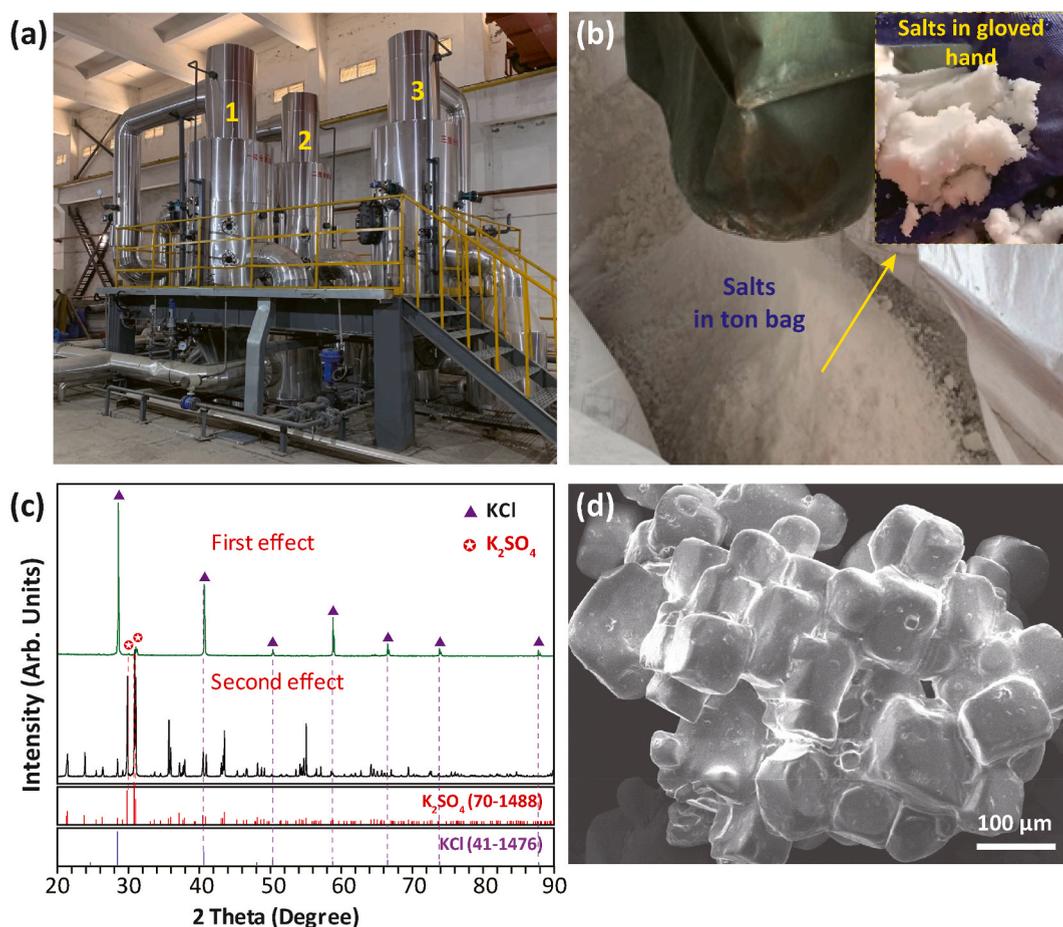


Fig. 7. Photos of the (a) salt-extraction device and (b) macroscopic morphology of extracted salts, (c) X-ray diffraction (XRD) patterns of the crystalline salts, and (d) the corresponding SEM morphology of the salts.

the filtrate will be transferred to the second-effect thickener, and after cooling, it will be sent to a centrifuge to separate the K_2SO_4 salts. The centrifuge mother liquor in the second effect is continuously fed to the evaporation chamber in the first effect where the KCl salts begin to crystallize from the liquid by cooling crystallization and subsequent salt collection by centrifugation. Along with the continuous extraction of KCl, Na^+ and residual heavy metal ions are gradually enriched in the small amount of remaining mother liquor. To prevent any remaining heavy metals in the KCl salts, the mother liquors are regularly pumped out of the system and into the cement kiln for calcination.

The vapor pressures of the first, second, and third effects are set to be 70 kPa, 50 kPa, and 23 kPa, respectively, while their liquid temperatures are designed to be 64 °C, 78 °C, and 95 °C, respectively. Besides, the crystallization temperature of both the first and second effects is 40 °C. By formulating this evaporation-extraction process, it is feasible to separate the K_2SO_4 salts from the second effect, and separate the KCl salts with high purity from the first effect. Therefore, by controlling the temperature zone and pressure for cooling crystallization in a triple-effect evaporation system, KCl salts can be effectively separated from other salts while reducing residual heavy metals in the salts.

3.3. Morphology and composition analysis of salt samples

A photograph of the three-effect salt-extraction device, macroscopic morphology of the extracted salt, XRD patterns of the crystallized salt samples, and the corresponding SEM morphology are presented in Fig. 7. As seen in Fig. 7 (a), the evaporation capacity of the salt extractor was 15 tons of saline/hour. The SEM morphology of the salt is shown in Fig. 7 (b), appearing as white crystalline powders. Combined with XRD patterns and SEM image as presented in Fig. 7(c–d), it can be determined that the salts that eventually separated from the first effect consists of mainly crystalline KCl salts (PDF No. 41–1476) and a very small amount of crystalline K_2SO_4 salts (PDF No.70-1488). As seen, the KCl crystals portray a regular cubic shape, with a grain size of approximately 35–135 μm . The above results demonstrate that the high-purity KCl crystal salts have been successfully extracted from the bypass dust.

To confirm the quality of the final extracted KCl salts, three samples were randomly selected during the continuous and stable operation of the system, and the contents of K^+ , Na^+ , Cl^- , SO_4^{2-} , and heavy metals in the samples were systematically determined using the ICP and titration methods. The results are presented in Table 4.

As shown in Table 4, K^+ (52.61–56.96 %) and Cl^- (42.01–43.68 %) had the highest contents in the final salt samples, followed by SO_4^{2-} (0.33–1.21 %) and Na^+ (0.18–0.55 %). Apparently, the sum of the K^+ and Cl^- content has exceeded 94 % of the weight of the salt. Combined with the above XRD analysis, we can conclude that the chemical composition of the final salt is mainly KCl (>90 %), with a small amount of K_2SO_4 . This indicates that high-purity potassium salts can be successfully extracted from the bypass dust. Note that the contents of all the heavy metal elements (e.g., Hg, As, Cd, and Pb) in the salt samples are less than 15 ppm. Importantly, the mass fraction of KCl salts obtained in this case is higher than 90 %, far exceeding the requirement that the mass fraction of industrial and agricultural potassium chloride must be greater than 60 % in the GB6549-2011 Potassium Chloride Standard. Moreover, the purity of the salts meet the requirements for the first-class potassium chloride in the GB/T 7118-2008 Industrial Potassium Chloride Standard, that is, the mass fraction of potassium chloride must be greater than 90 %. Therefore, the KCl salt obtained in this case is a first-class industrial potassium chloride salt with high economic value.

3.4. Economic benefit analysis

The environmental benefits of this work are obvious. Predictably, the economic effects are also significant for the sustainable development of the cement industry. In the following, the economic benefits of this case are briefly analyzed.

Specifically, the total investment in the bypass water washing and salt extraction project is about 10 million yuan, and the construction period is approximately one year. The operating costs of the project mainly include electricity fees, chemicals charges, evaporation heat consumption, labor costs, etc. The economic benefits brought by the project to the cement plant are estimated as follows: (1) Sales income of the KCl products. In this case, about 0.2 tons of KCl can be produced for every ton of the bypass dust. According to the KCl sales price of 2500 yuan/t, the annual income can be approximately $2500 \text{ (yuan/t)} \times 0.2 \text{ (t/t)} \times 30 \text{ (t/d)} \times 300 \text{ (d)} = 4.5$ million yuan. (2) The saved cost of the bypass dust sent for disposal as hazardous waste. If the bypass dust is transported out of the cement plant for hazardous waste disposal, the market price of this type of hazardous waste disposal would be 1000 yuan/t, and the annual savings benefit of this part would be $1000 \text{ (yuan/t)} \times 30 \text{ (t/d)} \times 300 \text{ (d)} = 9$ million yuan. (3) The considerable annual benefit from the project, which is estimated to be the sum of the sales income and the saved cost of the bypass dust, that is $4.5 + 9 = 13.5$ million yuan.

In addition to economic benefits, this project can also solve the problem of limited use of AFR in the kiln system due to the difficulty in disposal of high chlorine bypass dust and ensure the long-term stable operation of the AFR system. Therefore, this project can significantly reduce the overall energy consumption of the cement plant.

Very recently, Huaxin Cement Co., Ltd. successfully built and operated a new 120 t/d bypass dust washing and salt extraction system. The system can produce 24 tons of KCl products every day on average. This kiln line of the Huaxin Cement Co., Ltd. is almost the largest environmental co-disposal kiln line in China, and at present, its use of alternate fuels and raw materials is 2000 tons per day.

4. Conclusion

In this study, the successful collection of chlor-alkali rich bypass dust (30 t/d) from a cement kiln with a capacity of 4000 t/d has been achieved through the implementation of a proper bypass system. Moreover, we have made full use of the technical conditions of

Table 4
Quantitative analysis of elements in the final salt samples.

Element/ion	Unit	Sample 1	Sample 2	Sample 3
K ⁺	g/100g	56.96	53.51	52.61
Cl ⁻	g/100g	42.01	43.69	43.69
SO ₄ ²⁻	g/100g	1.21	0.61	0.33
Na ⁺	g/100g	0.18	0.38	0.55
Hg	mg/kg	<0.012	<0.012	<0.012
As	mg/kg	<15	<15	<15
Cd	mg/kg	<0.8	<0.8	<0.8
Co	mg/kg	<1.3	<1.3	<1.3
Cr	mg/kg	<1.8	<1.8	<1.8
Cu	mg/kg	<0.8	<0.8	<0.8
Mn	mg/kg	<1.1	<1.1	<1.1
Ni	mg/kg	<3.8	<3.8	<3.8
Pb	mg/kg	<10	<10	<10
Sb	mg/kg	<7.4	<7.4	<7.4
Zn	mg/kg	<13	<13	<13

cement production to create a comprehensive suite of industrial-scale treatment procedures and equipments, including chlorine-rich bypass dust washing and salt extraction. Regarding technological innovation, high-temperature flue gas containing CO₂ has been utilized to precipitate certain heavy metal ions, while steam from the waste heat power generation system has been employed as a heat source for the potassium salt evaporation process. Most excitingly, this novel industrial production line is capable of consistently extracting KCl salts from the bypass dust with high purity (over 90 %) and a daily yield of exceeding 6 tons. It is also worth noting that throughout the entire process, the output of the system is only valuable high-purity KCl products, and the remaining material is reintroduced into the cement kiln for calcination without additional contamination. Therefore, this work paves the way for cleaner production, carbon reduction, and resource utilization in the cement industry in the future.

Data availability statement

All relevant data that support the findings of this study are included in article referenced in this article. Furthermore, relevant data can also be provided by the corresponding author upon reasonable request.

Funding statement

This study had no funding support.

Ethics statement

Review and/or approval by an ethics committee was not needed for this study as it did not involve any medical research on humans, animals or other living beings in relation to ethical norms.

CRedit authorship contribution statement

Jiajun Wang: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing. **Pu Zeng:** Formal analysis, Writing – original draft. **Zhe Liu:** Data curation, Formal analysis, Methodology, Validation. **Yeqing Li:** Methodology, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Li Yeqing currently serves as a board member at Huaxin Cement Co., Ltd. He is also an adjunct professor at Wuhan University of Technology.

Acknowledgements

We acknowledge our colleagues at Huaxin Environmental Engineering Co., Ltd. for their experimental assistance in this work. We are also very grateful for the support of Huaxin Cement Laboratory Center in XRD, ICP-Mass and other test characterizations. We also sincerely thank Prof. Qiongzhen Liu for her helpful suggestions on the presentation of data and results.

References

- [1] M. Schneider, The cement industry on the way to a low-carbon future, *Cem. Concr. Res.* 124 (2019), 105792, <https://doi.org/10.1016/j.cemconres.2019.105792>.
- [2] D. Ferrario, S. Stendardo, V. Verda, A. Lanzini, Solar-driven calcium looping system for carbon capture in cement plants: process modelling and energy analysis, *J. Clean. Prod.* 394 (2023), 136367, <https://doi.org/10.1016/j.jclepro.2023.136367>.
- [3] Z. Ghoulah, Y. Shao, Turning municipal solid waste incineration into a cleaner cement production, *J. Clean. Prod.* 195 (2018) 268–279, <https://doi.org/10.1016/j.jclepro.2018.05.209>.
- [4] B. Reza, A. Soltani, R. Ruparathna, R. Sadiq, K. Hewage, Environmental and economic aspects of production and utilization of RDF as alternative fuel in cement plants: a case study of Metro Vancouver Waste Management, *Resour. Conserv. Recycl.* 81 (2013) 105–114, <https://doi.org/10.1016/j.resconrec.2013.10.009>.
- [5] Cembureau, Cementing the European Green Deal: Reaching Climate Neutrality along the Cement and Concrete Value Chain by 2050, The European Cement Association, Brussels, 2020. https://cembureau.eu/media/w0lbouva/cembureau-2050-roadmap_executive-summary_final-version_web.pdf.
- [6] H. Long, Y. Liao, C. Cui, M. Liu, Z. Liu, L. Li, W. Hu, D. Yan, Assessment of popular techniques for co-processing municipal solid waste in Chinese cement kilns, *Front. Environ. Sci. Eng.* 16 (2022) 1–13, <https://doi.org/10.1007/s11783-021-1485-4>.
- [7] W. Ma, T. Wenga, F.J. Frandsen, B. Yan, G. Chen, The fate of chlorine during MSW incineration: vaporization, transformation, deposition, corrosion and remedies, *Prog. Energy Combust. Sci.* 76 (2020), 100789, <https://doi.org/10.1016/j.peccs.2019.100789>.
- [8] P. Cholsaipant, J.L. George, D. Kim, A.A. Kruger, Volatility of sodium, potassium, and cesium perchlorates determined by thermogravimetry, *J. Therm. Anal. Calorim.* 147 (2022) 9291–9299, <https://doi.org/10.1007/s10973-021-11173-8>.
- [9] Y. Wang, H. Zhu, X. Jiang, G. Lv, J. Yan, Study on the evolution and transformation of Cl during Co-incineration of a mixture of rectification residue and raw meal of a cement kiln, *Waste Manage. (Tucson, Ariz.)* 84 (2019) 112–118, <https://doi.org/10.1016/j.wasman.2018.11.036>.
- [10] V. Kosajan, Z. Wen, K. Zheng, F. Fei, Z. Wang, H. Tian, Municipal solid waste (MSW) co-processing in cement kiln to relieve China's Msw treatment capacity pressure, *Resour. Conserv. Recycl.* 167 (2021), 105384, <https://doi.org/10.1016/j.resconrec.2020.105384>.
- [11] M.-X. Zhan, J. Fu, T. Chen, Y. Li, J. Zhang, X.-D. Li, J.-H. Yan, A. Buekens, Effects of bypass system on PCDD/F emission and chlorine circulation in cement kilns, *Environ. Sci. Pollut. Res.* 23 (2016) 19657–19666, <https://doi.org/10.1007/s11356-016-7082-6>.
- [12] K. Wojtacha-Rychter, M. Król, M. Golaszewska, J. Catus-Moszek, M. Magdziarczyk, A. Smoliński, Dust from chlorine bypass installation as cementitious materials replacement in concrete making, *J. Build. Eng.* 51 (2022), 104309, <https://doi.org/10.1016/j.jobbe.2022.104309>.
- [13] A.A. Ata, T.N. Salem, N.M. Elkhawas, Properties of soil–bentonite–cement bypass mixture for cutoff walls, *Construct. Build. Mater.* 93 (2015) 950–956, <https://doi.org/10.1016/j.conbuildmat.2015.05.064>.
- [14] N.T. Abdel-Ghani, H.A. El-Sayed, A.A. El-Habak, Utilization of by-pass cement kiln dust and air-cooled blast-furnace steel slag in the production of some “green” cement products, *HBRC J* 14 (2018) 408–414, <https://doi.org/10.1016/j.hbrj.2017.11.001>.
- [15] T. Hanein, Y. Hayashi, C. Utton, M. Nyberg, J.-C. Martinez, N.-I. Quintero-Mora, H. Kinoshita, Pyro processing cement kiln bypass dust: enhancing clinker phase formation, *Construct. Build. Mater.* 259 (2020), 120420, <https://doi.org/10.1016/j.conbuildmat.2020.120420>.
- [16] M. Daous, Recovery of potassium salts from kiln dust of local cement plants, in: The 6th Saudi Engineering Conference, KFUPM, Dhahran, Saudi Arabia, vol. 2, 2002, pp. 473–485, 14-17 December, <https://faculty.kfupm.edu.sa/COE/sadiq/proceedings/SEC2002/vol2/P473.pdf>.
- [17] K. Kim, Y. Chu, Study of using carbon dioxide for obtaining potassium chloride from cement by-pass dust, *Resour. Recycl.* 26 (2017) 38–44, <https://doi.org/10.7844/kirr.2017.26.6.38>.
- [18] M.-C. Han, D.-J. Lee, Physical and chemical properties of chlorine bypass system-dust from cement manufacturing, *J. Korean Recycl. Constr. Resour. Inst.* 7 (2019) 310–315, <https://doi.org/10.14190/JRCR.2019.7.4.310>.
- [19] A. Ullasz-BochenCzyk, Chemical characteristics of dust from cement kilns, *Gospod. Surowcami Miner. Resour. Manag.* 35 (2019) 87–102, <https://doi.org/10.24425/gsm.2019.128524>.
- [20] D. Okhrimenko, J. Nissenbaum, M. Andersson, M. Olsson, S. Stipp, Energies of the adsorption of functional groups to calcium carbonate polymorphs: the importance of –OH and –COOH groups, *Langmuir* 29 (2013) 11062–11073, <https://doi.org/10.1021/la402305x>.
- [21] Aqueous solubility of inorganic compounds at various temperatures, in: W.M. Haynes (Ed.), Section 5-Thermochemistry Electrochemistry and Solution Chemistry, in *CRC Handbook of Chemistry and Physics*, 95th Edition, CRC Press, Boca Raton, FL, 2014, pp. 1068–1073. <http://www.taylorandfrancis.com>.