

Article

Green Conversion of Coal Fly Ash into Soil Conditioner: Technological Principle and Process Development

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Abstract: White mud is residue discharged during the acid method in the aluminum extraction process from coal fly ash, and this material is harmful to the environment. The implementation of an environmentally friendly and valuable way to use white mud is a key factor restricting the commercial application of the acid method in the fly ash alumina extraction technology. An analysis of white mud revealed the following: (1) it was highly enriched in SiO₂ (70–80%) while concentrations of acid-soluble elements, such as Na, Al, and Fe, and some hazardous heavy metals, including Pb and Cr, were significantly lower than raw fly ash; (2) approximately 80% of SiO₂ had relatively high reaction activity because of the foregoing Al-extraction treatment. Through an ingenious green chemical process, the complete conversion of white mud into silicon–calcium fertilizer (SCF) was achieved under very mild reaction conditions (approximately 100 °C and atmospheric pressure). Waste liquor was totally recycled, and no secondary solid waste was generated. The SCF had an available silicon content (ASC) of 35%, significantly higher than the commercial standard (20%). Converting them into soil conditioners or ecological remediation materials with the lowest possible energy consumption and secondary pollution may be the most promising approach for the future disposal of aluminosilicate industrial solid wastes.

Keywords: fly ash utilization; heavy metal elements; available silicon; one-step hydrothermal activation; soil remediation



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1. Introduction

High alumina coal and coal combustion fly ash in the Zhungeer coal basin in China, a “unique polymetallic artificial deposit,” has attracted increasing attention [1–5]. The amount of aluminum in this high-Al coal and fly ash is estimated to be as high as 10 billion tons of Al₂O₃. Development of high-Al fly ash is of great importance in reducing China’s excessive dependence on bauxite resource importing.

Attempts to recover aluminum from fly ash can be traced back to the 1950s [6]. Recovery technologies for aluminum from fly ash include the Bayer method (1) [7], a high-temperature chlorination process (2) [8], and the acid-leaching method (3) [9]. So far, many researchers and engineers have made improvements to these three systems [10,11]. Using the Zhungeer high-Al circulating fluidized bed fly ash as a raw material, the China National Energy Group developed and successfully applied the enhanced one-step hydrochloric-acid-leaching method to produce a metallurgical grade alumina product; the recovery rate of aluminum is up to 85% [12]. More importantly, volume of the secondary solid waste (commonly known as white mud) discharge is only one-third of that generated by the alkali method. A fly ash alumina extraction (FAAE) semi-industrial plant (125 kt of Al₂O₃, annually) is currently in the design and construction stage. Future progress of acid corrosion resistance technologies will ensure HCl acid leaching as the most promising method for FAAE. Nevertheless, when this plant begins production, approximately 180 kt of HCl-bearing white mud will be generated, requiring safe disposal. China is currently

searching for cleaner industrial production and a more efficient model for economic growth. Therefore, environmentally friendly and valuable utilization of white mud is a key factor restricting the commercial application of the acid method in FAAE technology.

A promising strategy has been proposed to transform harmful white mud into an ecological restoration material: silicon–calcium fertilizer (SCF). Traditional chemical fertilizers are predominantly used to supplement major nutritional elements, such as nitrogen, phosphorus, and potassium; this results in a deficiency in medium or micro elements, especially the available silicon. The effects of silicon nutrients on improving soil structure, passivating heavy metals, and increasing yield and quality of agricultural products have been widely confirmed [13–17]. In fact, the use of silicon as a nutrient has been widely studied in tropical regions and for rice production around the world, specifically in India [18,19], Japan [20], and China [21,22]. Cheap and efficient silicon fertilizer products are urgently needed in the market. Currently, approximately 50% of paddy rice soils in China are Si-deficient; the annual shortfall in demand for silicon fertilizer in the Chinese market is estimated to be up to 40 million tons, offering tremendous space for the disposal demand of white mud or other similar solid wastes.

Research on the production and application of SCF or soil conditioner directly using fly ash as a raw material has been in progress and has become a hot spot. Silica gels obtained from coal ash by the alkali–acid (NaOH–HCl) chemical method were used to make SCF, with available silicon content (ASC) values ranging around 30% [23]. After mixing with the equal mole Ca(OH)₂ powder and hydrothermally reacting (200 °C) in 0.6 mol/L KOH solution for 5 h, fly ash can be transformed into a soil conditioner product with an ASC = 35% [24]. However, the suspicion of ecological safety caused by excessive heavy metal content in fly ash has never disappeared [25,26]. This is also the key factor restricting the combination of fly ash utilization and soil remediation. On the other hand, how to significantly reduce the cost of fly ash SCF production, mainly the energy consumption, is the primary technical direction, which determines if this technology can be commercialized.

This work aims to convert white mud into a high-quality SCF product through an innovative green process that is expected to provide a feasible approach for the economically sustainable and ecological application of the coal fly ash resource.

2. Materials and Methods

2.1. Materials

The raw materials used in this study were collected from the FAAE demonstration plant in Zhungeer, Inner Mongolia, China. After drying, the ash yield elements and mineral composition of the white mud samples were determined by X-ray fluorescence spectrometry (XRF, ZSX Primus, Rigaku, Japan) and X-ray diffraction (XRD, D8 ADVANCE, Bruker, Germany). As shown in Table 1, white mud is predominately composed of SiO₂ (78.7%), Al₂O₃ (13.4%), and TiO₂ (5.2%). Concentrations of acid-soluble elements, such as Na, Al, and some heavy metals, are much lower than that of the parent material (fly ash) because of the acid-leaching process. Enrichment of the SiO₂ and dilution of the Al₂O₃ facilitates the production of high-quality SCF. This is also why traditional SCF manufacturing would previously select high-cost feldspar ore (SiO₂ = 64.7%, Al₂O₃ = 18.4%) as a raw material rather than clay minerals (e.g., kaolinite, SiO₂ = 46.5%, Al₂O₃ = 39.5%) even though clay materials are much cheaper and more readily available.

Table 1. Elemental composition (ash base) of white mud and the alkali-leaching desiliconized white mud (%).

	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	Na ₂ O	CaO	TiO ₂	Fe ₂ O ₃	ZrO ₂
High-Al fly ash	52.5	38.1	0.31	0.64	0.55	0.06	2.11	2.81	2.10	0.18
White mud	13.4	78.7	0.14	0.35	0.16	bdl ¹	0.37	5.2	0.45	0.29
Desiliconized white mud [27–29]	56.7	23.2	0.1	0.67	0.12	3.44	0.95	11.7	1.71	0.48

¹ below the minimum detection limit.

Available silicon content (ASC) in soil is drastically different from the unavailable silicon that cannot be absorbed and used by crops; ASC is the most critical indicator of silicon fertilizer. The commercial standard for silicon fertilizer in China is $ASC \geq 20$ wt%. A higher ASC value demands a higher product selling price. Therefore, the key to preparing silicon fertilizer is converting unavailable silicon into the available form while minimizing the cost of materials and energy consumption.

Previous white mud desilicization studies [27–29] conducted by our team indicated that more than 80% of the silicon in white mud is extractable by NaOH alkali leaching, and we referred to this portion of silicon as active silicon. In combination with the X-ray diffraction (XRD) analysis (Figure 1), active silicon is inferred to come from amorphous glass; this percentage can be characterized by the integrated intensity of the dispersion peak existing in the $2\theta = 15^\circ$ – 35° section of the XRD spectral line.

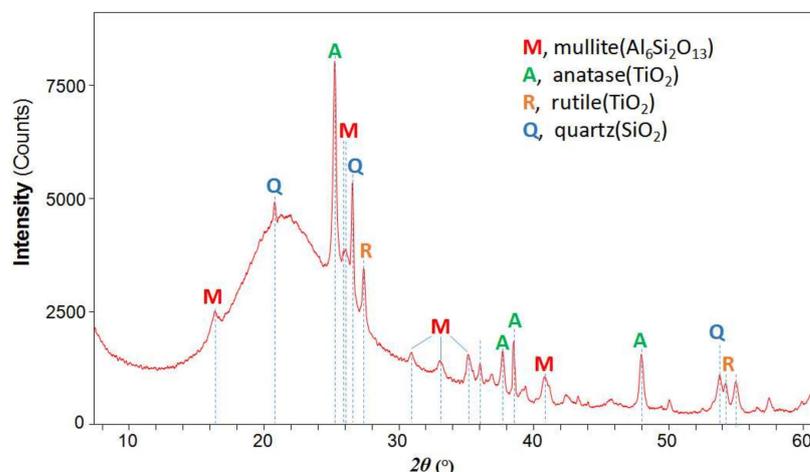


Figure 1. Mineral composition of white mud based on XRD analysis.

In addition to amorphous glass, the mineral composition of white mud includes mullite, quartz, anatase, and rutile. Carrier minerals for Al_2O_3 and SiO_2 are mainly mullite ($3Al_2O_3-2SiO_2$) and quartz (SiO_2) while the carrier minerals for TiO_2 are anatase and rutile. These crystal minerals all have a highly stable crystal structure, which ensures they can be preserved and enriched after high-temperature acid leaching.

These minerals also show no reaction in the alkali-leaching desilicization experiments mentioned above. In contrast to the active silicon in amorphous glass, the silicon in crystal minerals is referred to as inactive silicon. The theoretical energy consumption for the conversion from active silicon to available silicon is significantly lower than that of inactive silicon to available silicon. In this study of a low-cost production method of SCF from white mud, only the active silicon will be activated and converted while inactive silicon will not participate in the activation reaction.

2.2. Technique Principle and Methods of Silicon Activation

The current SCF production technology uses the calcining activation method ($1300^\circ C$ heating for 30 min) of potash feldspar. Research on reducing the costs of raw materials and energy consumption has not produced significant improvements. Some researchers have attempted the autoclaved activation method to produce silicon–calcium–potassium fertilizer, with an acceptable activation efficiency. For example, Liu Jianming et al. [30–32] successfully produced Si–Ca–K fertilizer with $ASC > 20\%$ from potassium feldspar and $Ca(OH)_2$ powder as raw materials by autoclave activation at $190^\circ C$ for 8–12 h in a closed vessel. However, the reaction pressure could reach 1.25 MPa, leading to a considerable increase in costs for equipment investment and production operation.

Luo and Wu (2021, Preprint) published their work on the preparation of silicon fertilizer using the residue from alumina extraction of coal fly ash by decomposing the main

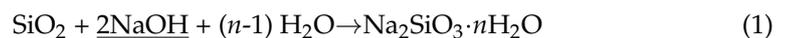
mineral phase $[\text{NaCaHSO}_4]$ under an alkali hydrothermal environment ($\text{Na}_2\text{O} = 30 \text{ g/L}$, $\text{L/S} = 25$, $150 \text{ }^\circ\text{C}/4 \text{ h}$) [33]. Although its topic ASC value reached 28.75%, the high temperature and pressure operating conditions and a high L/S may still not be suitable for the industrial production.

Based on the characterization and experimental analysis mentioned above, efficient conversion of active silicon in white mud into available silicon can be realized under a mild hydrothermal reaction situation (e.g., approximately $100 \text{ }^\circ\text{C}$, at atmospheric pressure; $\text{SiO}_2 + 2\text{NaOH} + (n-1)\text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 \cdot n\text{H}_2\text{O}$). However, this process could cause excess sodium and high pH in the final product; the application of this product to soil would increase the risk of salinization and alkalization. Additionally, the reaction product is too viscous to be filtered and dried because of the presence of water glass ($\text{Na}_2\text{SiO}_3 \cdot n\text{H}_2\text{O}$).

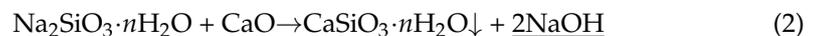
Calcium is an essential nutrient for crops. $\text{Ca}(\text{OH})_2$ was evaluated as a substitute for NaOH as an activator. Unfortunately, no acceptable activation efficiency could be achieved under atmospheric pressure using $\text{Ca}(\text{OH})_2$ even when the reaction temperature was increased above $160 \text{ }^\circ\text{C}$. The reactive activity of Ca is much lower than Na , which is why the calcination temperature and energy consumption cannot be significantly reduced with a calcium-based activator.

To solve the above technical challenge, an innovative technique principle for silicon activation was developed:

1. In an atmospheric pressure hydrothermal environment, NaOH was first reacted with the active silicon in white mud (Equation (1)).



2. CaO powder was synchronously added to the reaction system and continued to react with $\text{Na}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$ produced in Step 1.



3. NaOH participated in the whole reaction as a catalyst and was not consumed (Equation (2)). The NaOH solution was easily recovered and recycled in the next round of the reaction, ensuring the minimization of alkali cost and the alkalinity residue in the final product. Therefore, Equations (1) and (2) can be merged into a single equation (Equation (3)).



Based on this new reaction principle for silicon activation, white mud SCF can be obtained through a one-step hydrothermal activation procedure, shown in Figure 2.

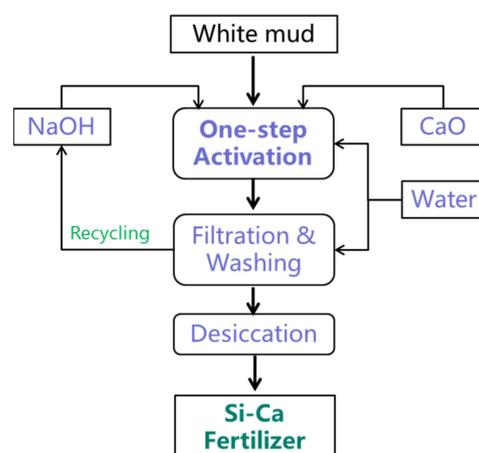


Figure 2. Technical process for the preparation of white-mud-based SCF.

In order to rapidly define the appropriate range of reaction conditions, orthogonal experiments ($L_9 3^4$) were carried out by focusing on four factors (three levels for each factor): activating temperature ($T = 90\text{ }^\circ\text{C}$, $100\text{ }^\circ\text{C}$, $120\text{ }^\circ\text{C}$), reaction time ($t = 2\text{ h}$, 3 h , 4 h), activator type ($AT = \text{I, II, III}$), and the mass ratio of liquid (water) to solid (white mud) ($L/S = 6, 10, 20$). Activator Type I, II, and III represent different ratios of Ca–Mg–Na–K, respectively.

2.3. Analysis Method for SCF Product

A field emission scanning electron microscope (SEM, Nova NanoSEM, FEI, USA) was used to obtain information about the micromorphological information of the white mud SCF product. A laser particle size analyzer (Master sizer 2000, Malvin Instrument, Cambridge, UK) was used to analyze the overall fineness and particle size distribution of the SCF.

The ASC and available CaO content (ACC) for the SCF samples were determined using the Chinese Standard NY/T 2272, which has been described in detail by Hu et al. (2015) [34]. The sample was mixed with a $150\times$ (mL/g) HCl solution (0.5 mol/L) and oscillated at $30\text{ }^\circ\text{C}$ for 80 min. After this reaction, the filtrate was obtained to determine the dissolved silica content. The percentage of the soluble SiO_2 (CaO) mass of the total sample mass was equivalent to the ASC (ACC) value.

3. Results

3.1. Optimal Parameters for the Hydrothermal Activation

An extremum difference analysis of the orthogonal experiments data, as listed in Table 2, indicated that the degree of influence of the hydrothermal activation factors on ASC occur in descending order: $AT > T > L/S > t$. The proper composition of the activator is the most important factor for effective silicon activation. Not surprisingly, reaction temperature and time also played crucial roles in hydrothermal systems. However, a delicate balance of temperature and time is clearly needed. An inadequate activation energy input (e.g., $T = 90\text{ }^\circ\text{C}$, $t = 2\text{ h}$) led to an insufficient reaction (Equation (3), Section 2.2), which was easily understood, but increasing the reaction temperature (e.g., $T = 120\text{ }^\circ\text{C}$) or time (e.g., $t = 4\text{ h}$) further brought about a decrease instead of a rise in ASC. That is because the hydrothermal activation of amorphous SiO_2 in fly ash or similar heat-treated aluminosilicate solid waste (including white mud) partially overlaps with the reaction conditions for hydrothermal crystallization of zeolites; as the activation conditions shift toward crystallization conditions, the elements Al and Na, instead of Ca, prefer to rebind with the activated Si released from the amorphous glass, resulting in an excessive generation of zeolites [35–37] (Figure 3A vs. Figure 3B). The occurrence of this side reaction decreased both the ASC value of the final products and the recovery or cycle rate of Na. A smaller L/S in industrial production would increase production efficiency and reduce pressure of wastewater treatment; therefore, $L/S = 10$ was also considered acceptable since the mean ASC value (K_i) of $L/S = 10$ (26.58%) was only slightly lower than $L/S = 20$ (27.87%).

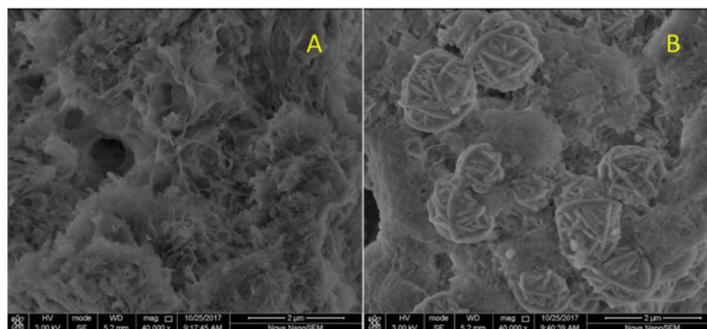
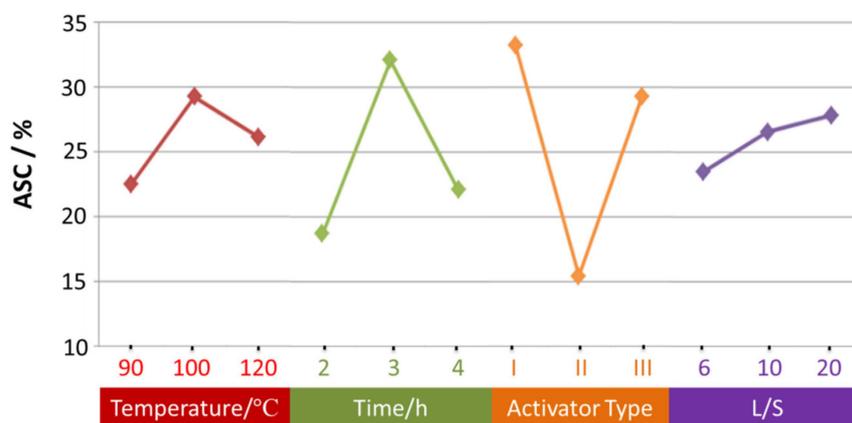


Figure 3. SEM images of the white-mud-based SCF products: (A) No. 6 sample with lamellar structure; (B) No. 9 sample with excessive zeolite crystals.

Table 2. Conditions and test results from the hydrothermal activation $L_9 3^4$ orthogonal experiments.

No.	Temp./°C	Time/h	Activator Type	L/S	ASC/%
1	90	4	I	6	27.18
2	90	2	II	10	11.94
3	90	3	III	20	28.38
4	100	4	II	20	20.50
5	100	2	III	6	29.44
6	100	3	I	10	37.86
7	120	4	III	10	29.93
8	120	2	I	20	34.73
9	120	3	II	6	13.88
K_1	22.50	25.71	33.26	23.5	
K_2	29.27	25.37	15.44	26.58	
K_3	26.18	26.71	29.25	27.87	
$R = \max\{K_i\} - \min\{K_i\}$	6.767	1.337	17.817	4.370	

The effect curve (Figure 4) of each factor based on the mean value of each experimental level was drawn to make a visual analysis for finding the best level. Eventually, the gram-scale optimal parameters were determined as ($T = 100$ °C, $t = 3$ h, $AT = I$, and $L/S = 10$ – 20), which happened to appear in the No. 6 experiment listed in Table 2. Its ASC value reached 37.86%, much higher than the commercial standard for silicon fertilizer in China ($ASC \geq 20\%$). The ACC value reached 34.79% for the same sample. Therefore, high-performance SCF products were produced by this process.

**Figure 4.** Effect curves of the $L_9 3^4$ orthogonal experiments of white mud SCF production.

Aluminum and sodium are two unfavorable factors for SCF because these two elements are already present in excess in the soil. In this study, soluble Al_2O_3 and soluble Na_2O in products prepared under diverse experimental conditions were also monitored (Table 2).

Single-factor experiments were further carried out around the optimal parameters. During the process of actual operations, it was discovered that the insufficient addition of Ca resulted in the presence of Na_2SiO_3 (Equation (1), Section 2.2), making it difficult to execute the filtration, washing, and drying, and caused filtration losses of Si and Na. Although Ca is a nutrient for crops, a superabundant Ca addition will dilute the ASC index of the SCF product. Superfluous $Ca(OH)_2$ would also cause an unwished high pH value of the final product.

3.2. Kilogram-Scale Verification Experiments for SCF Production

Based on the optimized process parameters obtained from the above gram-scale experiments, SCF preparation experiments at the kilogram scale were carried out using a

5 L double-layer glass reactor. Through several additional experiments, the reaction time and the L/S value were adjusted to 3.5 h and 8, respectively. To achieve the reuse of alkali and water to save material costs and reduce secondary pollution, the produced waste lye from reaction Round I was collected and reused in Round II and again in Round III. During this process, almost no secondary solid waste was discharged.

As shown in Table 3, the ASC values of the SCF products from Rounds I to III vary from 35.05 to 37.60%, almost meeting the best performance data achieved in the gram-scale experiments (37.86%); the ASC value is also much higher than the commercial silicon fertilizer standard (20%). The ACC values of three samples also exceeded the commercial standard of 28%.

Table 3. Technical Index of SCF products prepared from the kilogram-scale lye-cycle experiments.

	ASC/%	ACC/%	Heavy Metal Elements (ppm)				
			Cr	Cd	Pb	Hg	As
Round I	36.36	29.99	14.45	0.22	19.18	3.91	2.83
Round II	35.05	31.17	15.91	0.25	20.50	4.00	3.00
Round III	37.60	29.78	16.71	0.24	21.09	2.81	3.56
Standard [38]	≥20	≥28	≤500	≤10	≤200	≤5	≤50

The last remaining criteria to determine if the produced products could be used as commercial SCF was whether the heavy metals (Pb, Cr, Cd, Hg, As) exceeded the corresponding limits. The heavy metal contents of the three products are all below the required magnitude by the Chinese standard [38]. Therefore, the products are initially identified as an ecologically safe and high-performance SCF product.

3.3. Detailed Characterization of the White Mud SCF

The typical microtopography of SCF is a lamellar structure with low crystallinity (Figure 3A), with the chemical components of Ca–Si–H–O. White mud SCF possesses excellent fineness (Figure 5, $D_{v50} = 17.9 \mu\text{m}$) and a microscopic porous structure, which contribute to the overall high-specific surface area and absorbability. These characteristics help in the conservation and slow release of nutrients and moisture and are also conducive to the adsorption and deactivation of heavy metals in soil. Porous, unburned carbon inside the SCF may also increase the specific area and adsorptive properties.

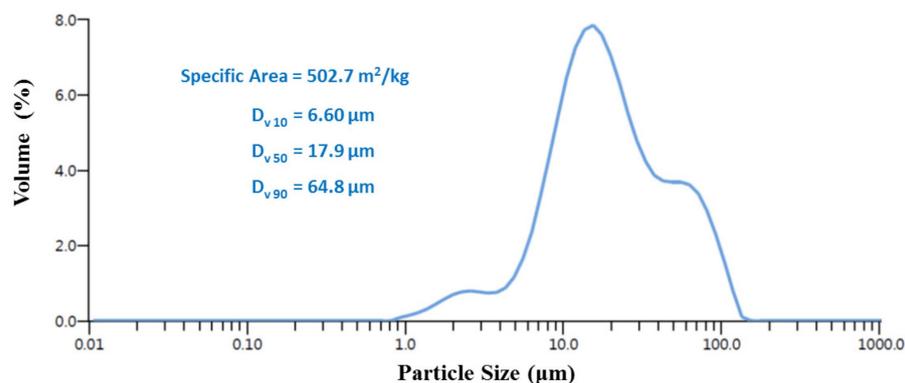


Figure 5. Laser particle size distribution of the white mud SCF product powder.

The cation exchange capacity (CEC, cmol/kg) is the molar number of all exchangeable cations (i.e., K^+ , Na^+ , Ca^{2+} , NH_4^+ , H^+ , Al^{3+}) in the soil. A higher CEC value indicates that more nutrients can be preserved in the soil. The CEC is commonly used as a key index to evaluate soil fertility. Although there is no mandatory standard for the CEC in SCF or soil conditioner products, the soil's CEC index can be directly and effectively increased when the soil conditioner product has a significantly higher CEC. Therefore, the CEC levels of

SCF samples produced in this experiment compared with those of commercial calcination products using the test method published by the China Environmental Industry Standard (HJ889-2017) for soil. Data (Table 4) indicated that our product had a significantly higher CEC than the purchased product.

Table 4. Cation exchange capacity (CEC) of SCF products produced by various activation methods.

Samples	ASC (%)	ACC (%)	CEC (cmol/kg)
White mud—hydrothermal-activated SCF	37.6	29.8	38.26
Potash feldspar—autoclave-activated SCF (commercial product)	20.0	25.0	45.0
Potash feldspar—calcination-activated SCF (commercial product)	26.0	24.9	5.53
General Chinese farmland soil	-	-	10–20

The CEC is also the main source of the soil buffering capacity for harmful Na^+ , Al^{3+} , heavy metals, and pH [39,40]. When the $\text{CEC} \geq 20$ cmol/kg, soil has a stronger heavy metal antagonism ability. The CEC of general Chinese farmland soil varies from 10 to 20 cmol/kg; at a value of $\text{CEC} \leq 5$ cmol/kg, the upper limit of soil heavy metal content is reduced by half (Chinese Soil Environmental Quality Standard, GB 15618-1995). SCF generated by the calcination method with a poor CEC (5.53 cmol/kg) does not show a direct improvement of the soil's CEC. In contrast, the hydrothermal SCF product with a significantly higher CEC level (38.26 cmol/kg) should have a higher potential to improve soil.

Soil is derived from the natural weathering of upper crust rocks; therefore, soil and rocks are homologous in terms of elemental composition. Coal is also a type of rock enriched in organic matter. Crushing and grinding, burning (thermal activation of crystal minerals), acid method alumina extraction (geological eluviation), and SCF production (alkali hydrothermal alteration) all simulate the natural processes of soil formation. Therefore, these processes follow the natural pathways for soil formation but at a higher rate. Therefore, it is understandable that the hydrothermal SCF products have comprehensive advantages. This technical solution could also be applicable to similar geological solid wastes, such as fly ash, coal gasification slag, and steel slag. Preliminary calculations indicate that the production cost of white mud SCF through the proposed atmospheric-pressure and low-temperature hydrothermal activation method can be controlled at US \$60, approximately two-thirds the cost of existing technologies.

4. Conclusions

Some inherent superiority on the elemental and mineral composition of white mud, such as being Si-rich, ecologically safe from a heavy metal aspect and easily activated, were discovered and fully utilized in this work. An innovative, low temperature and atmospheric pressure hydrothermal activation process ($T = 100$ °C, $t = 3.5$ h, $AT = I$, and $L/S = 8$) on a kilogram scale was developed, with low energy consumption, low material cost, and high-efficiency activation of silica. Experiments indicated that white mud can be 100% converted into a high-performance SCF product with good fineness ($Dv50 = 17.9$ μm), an abundant porous structure, and a high CEC (38.26 cmol/kg). In particular, the core quality index ASC can reach 35.05%–37.60%, about 80% higher than the commercial silicon fertilizer standard ($ASC = 20\%$). All of these features would contribute to the actual effects of white mud SCF products, such as conservation, the slow release of nutrients and moisture, adsorption and fixation of heavy metals in soil, etc.

Conversion of industrial solid wastes into soil conditioners supports agricultural development and ecology preservation with minimal cost and may also provide a promising direction for the utilization of similar aluminosilicate industrial wastes (e.g., fly ash, coal gasification slag, coal gangue, alumina red mud) in the foreseeable future.

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