Supporting Information

Convert hazardous Fluorine-containing sludge into monodisperse, highly crystalline, and acid-grade CaF2 nanomaterials via digestive ripening under acid-enhanced hydrothermal treatment

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Text S1.SEM of the raw material FCS.

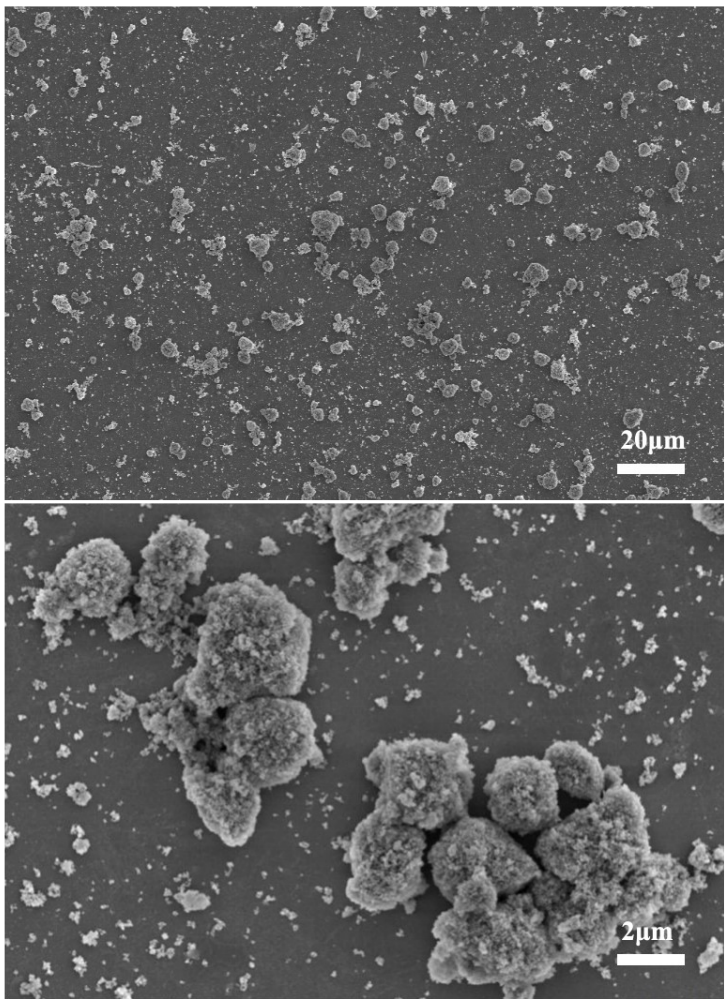

Fig. S1 SEM of the raw material FCS.

From the SEM images, it can be observed that the particles in the fluorine-containing sludge sample were very small, with a particle size ranging from approximately 20-80 nm. The particles had a low degree of crystallinity and primarily exhibit a flocculent aggregate morphology, with the size of these aggregates around 5-10 μm, along with some nanoscale particles.

Text S2.XPS of the raw material FCS.

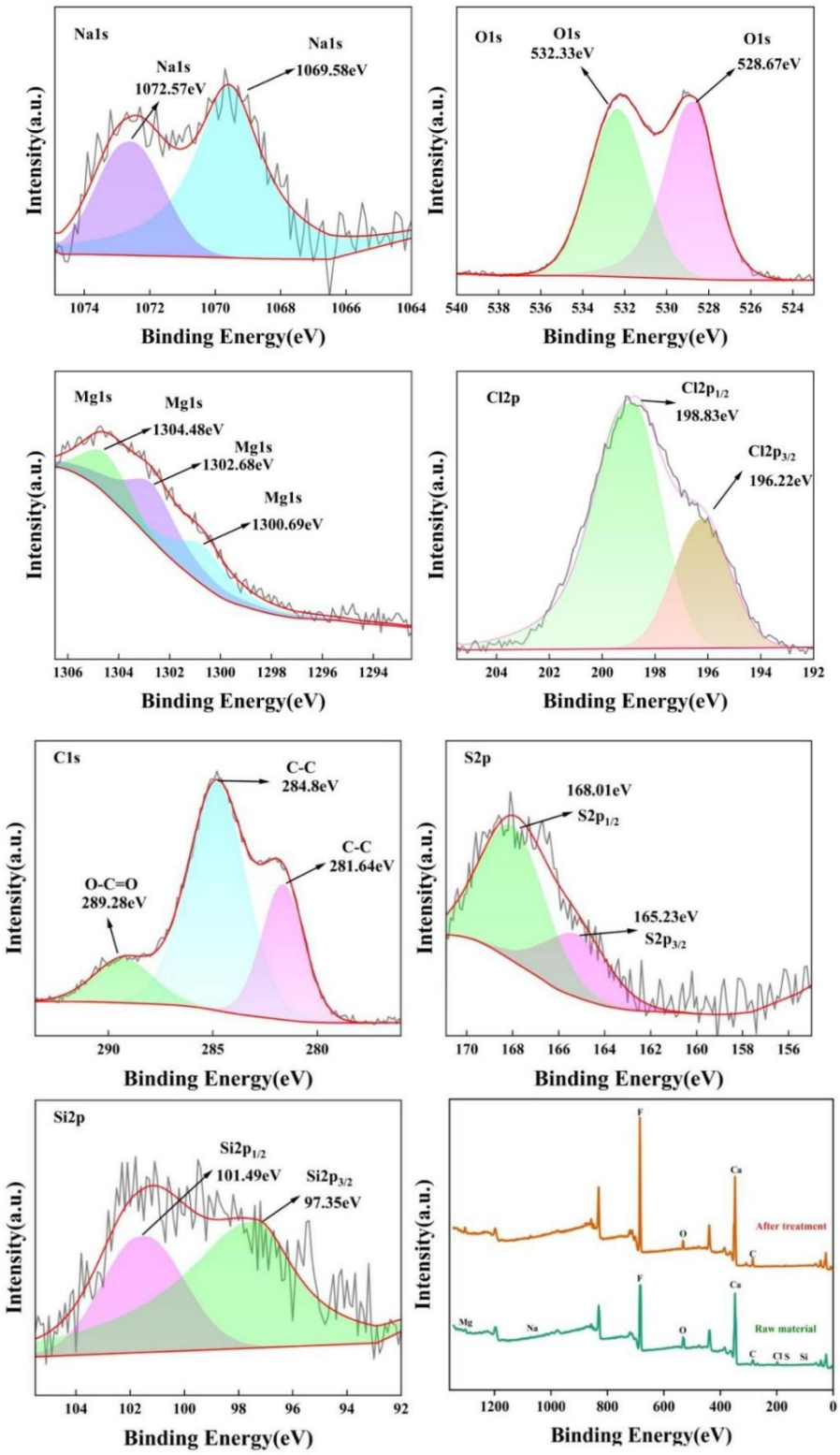

Fig. S2 XPS spectra and valence state analysis of FCS.

XPS analysis in FigS1 indicated that N, C, S, and Si in FCS exist in the +5, +4, +6, and +4 oxidation states, respectively. Additionally, Raman and FT-IR spectra in Fig6 and FigS3 showed that N, C, and S in FCS were combined with O to form NO_3^-, CO_3^{2-}, and SO_4^{2-}. Furthermore, based on Table 1 and the actual process of fluorine-containing wastewater treatment, it was inferred that the main impurity phases in FCS were $NaNO_3$, $CaCO_3$, $CaSO_4$, $MgCl_2$, SiO_2, and NaCl.

Text S3.TG of the raw material FCS.

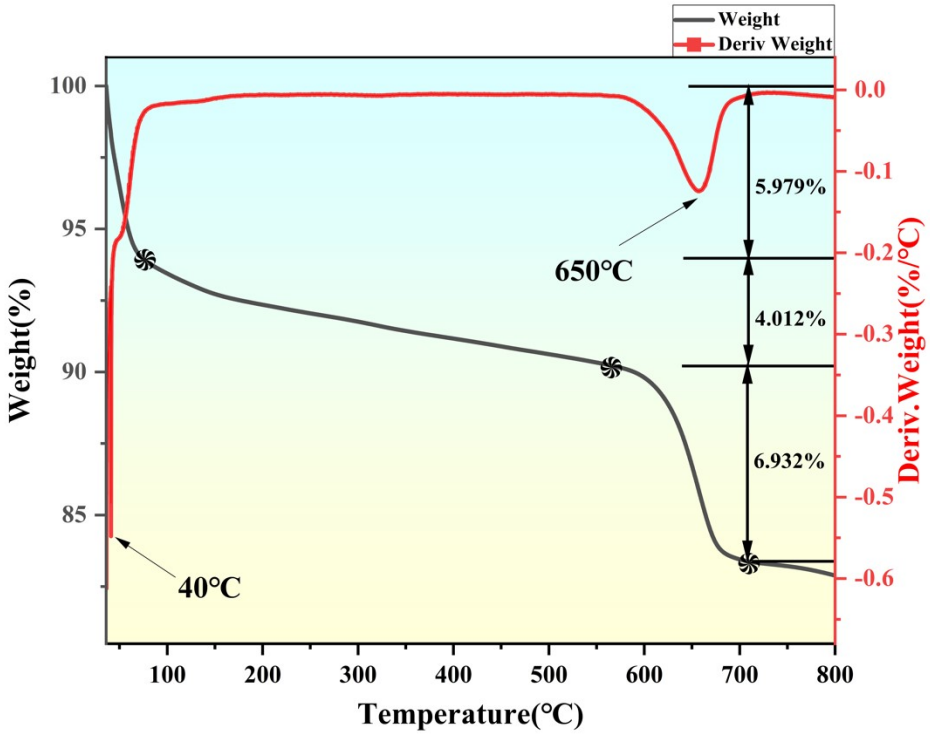

Fig. S3 TG of the raw material FCS.

The TG analysis of fluorine-containing sludge (FCS) revealed three main stages of weight loss. The first stage, with a weight loss of 5.979%, occurred between 30-105 °C, with an endothermic peak at 40 °C, primarily due to the evaporation of water absorbed on the surface of FCS. The second stage of weight loss occurs between 105-550 °C, which is likely due to the organic impurities, with a weight loss of 4.012%. The third stage, occurring between 550-720 °C, with an endothermic peak at 650 °C, corresponded to the thermal decomposition of $CaCO_3$, producing CaO and CO_2. The escape of CO_2 gas leads to the weight loss, with CO_2 accounting for 6.932%.

Text S4.Raman spectra of FCS and the solid products after treatment.

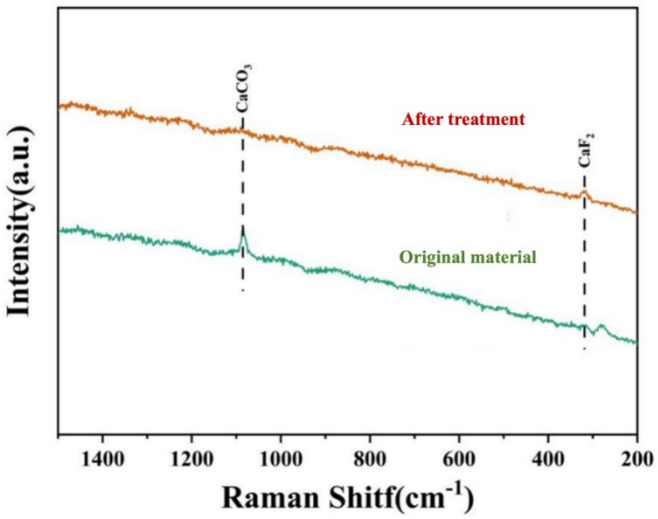

Fig. S4 Raman spectra(d)of FCS and the solid products after hydrothermal reaction.

The Raman spectrum showed a distinct peak around 1085 cm^{-1} in the untreated sample, corresponding to the symmetric stretching vibration of $CaCO_3$. After treatment, this peak disappeared, further confirming the removal of $CaCO_3$ as suggested by the infrared spectrum. In the treated sample, a new peak appeared around 415 cm^{-1}, which corresponded to the characteristic peak of CaF_2, indicating that the purity of CaF_2 after the reaction treatment is high. The combined analysis of these two spectra demonstrated that the hydrothermal treatment process not only effectively removed impurities but also promoted the formation and purification of CaF_2, making the treated sample meet the requirements for high-purity CaF_2.

Text S5.Changes in the percentage of organic elements before and after treatment.

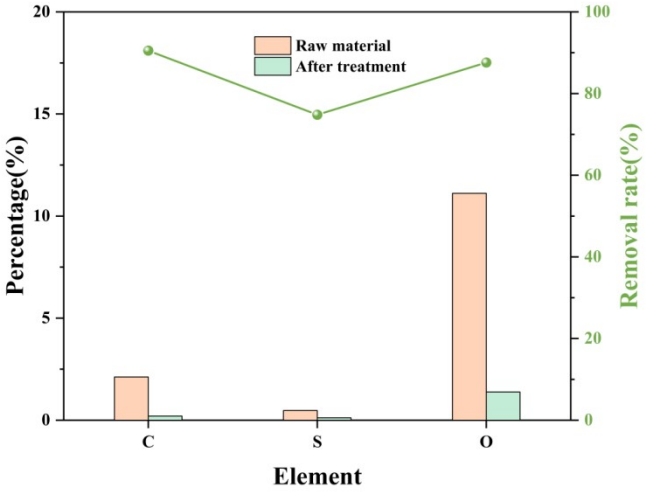

Fig. S5 Changes in the percentage of organic elements before and after treatment.

Before treatment, the carbon (C) content was 2.12%, indicating a significant presence of organic matter in the fluorine-containing sludge. Carbon is a key element in organic compounds, and the high carbon content before treatment suggests the presence of various organic compounds, such as organic acids, humic substances, or other carbon-containing pollutants. After treatment, the carbon content drastically decreased to 0.2011%, a reduction of approximately 90%. This indicates that the hydrothermal treatment was highly effective in removing organic matter. Hydrothermal reactions typically occurred under high temperature and pressure conditions, which can effectively break chemical bonded in organic matter, causing it to decompose into small molecular gases (such as CO_2, methane, etc.) or other volatile products that escape from the system. Thus, the reduction in carbon content directly reflected the significant decomposition and removal of organic matter during the hydrothermal treatment process. Before treatment, the oxygen(O)content was 11.11%, indicating the presence of significant amounts of oxides and organic compounds in the sludge. Since organic matter often contains oxygen functional groups(such as carboxyl and hydroxyl groups),the oxygen content can also serve as an indirect indicator of the organic matter content in the sludge. After treatment, the oxygen content significantly decreased to 1.37%,further demonstrating that oxygen functional groups in organic

matter were decomposed or converted into volatile oxides, such as CO_2 and CO, which were expelled as gases. Before treatment, the sulfur (S) content was 0.47%. Organic sulfur compounds were a major form of sulfur in organic matter, with compounds such as mercaptans and organosulfur compounds possibly presented in the sludge. After treatment, the sulfur content reduced to 0.12%, showing that sulfur compounds were effectively removed during the hydrothermal treatment. Organic sulfur compounds were likely converted into gases such as SO_2 or H_2S, which volatilized, or were oxidized into soluble sulfates and removed from the liquid phase. Through various chemical reactions, the organic matter in the fluorine-containing sludge was decomposed and removed. Pyrolysis broke the chemical bonds of carbon-hydrogen and carbon-oxygen, generating small gaseous molecules like CO_2, CH_4, and H_2 that were volatilized. Organic matter underwent oxidation under high temperature and pressure, producing gaseous substances like CO_2 and SO_2. Additionally, organic matter was hydrolyzed to form small, water-soluble organic acids, which were further decomposed or dissolved into the aqueous phase.

Text S6.Reuse and Characterization of Wastewater.

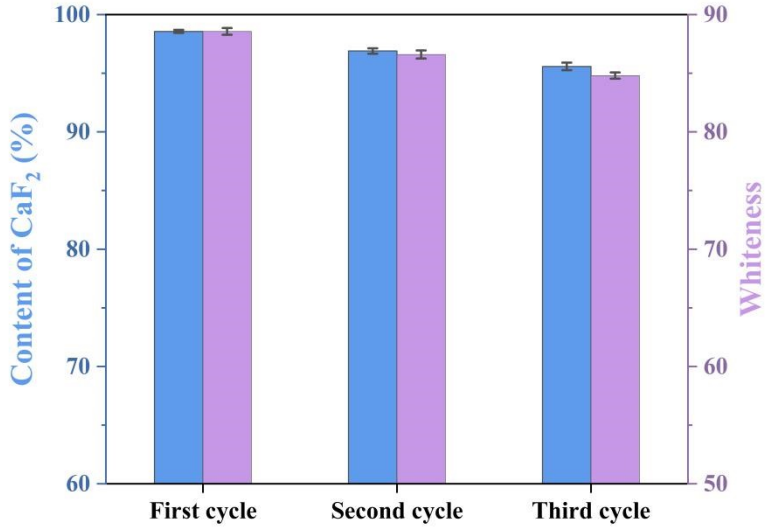

Fig. S6 The Reuse Effectiveness of Wastewater After Acid Supplementation

5ml/L of the HF was added to the used wastewater. Although the purity of CaF_2 in the samples after waste liquid reuse decreased, the overall effect was still effective. After three cycles, the purity of CaF_2 remained above 95%, and the whiteness reached above 84, indicating a certain reuse value. This process not only conserved water resources but also recovered a portion of the fluorine resources.

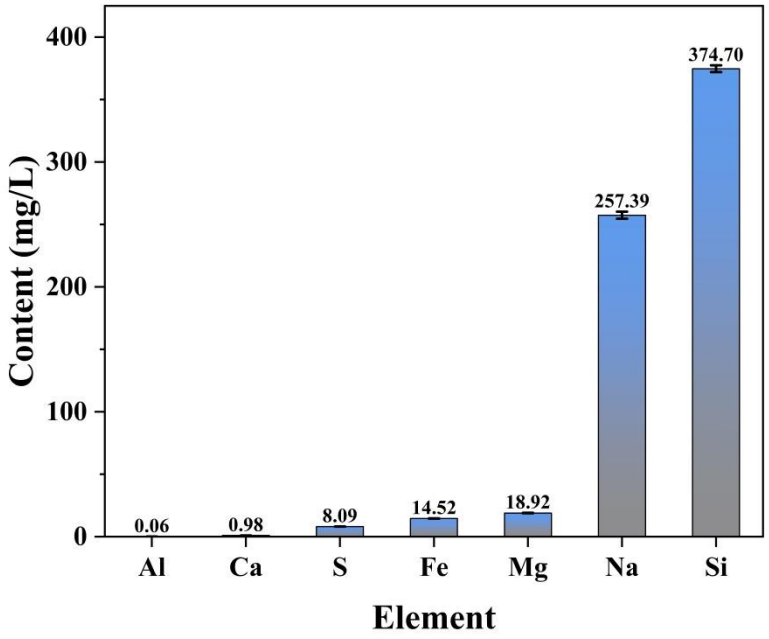

Fig. S7 Characterization of Elements in Wastewater by ICP

The used wastewater was characterized by ICP, and it was found to contain a variety of impurity elements. The repeated reuse of waste liquid inevitably leads to the accumulation of soluble impurities in the solution. Therefore, pH neutralization and calcium salt precipitation treatment are still required in the end, and advanced treatment is carried out to ensure compliance with discharge standards. Future research will further optimize waste liquid reuse strategies to improve resource recovery rates and reduce environmental impacts.