Article

Design of an Exploratory Experiment in Teaching for Engineering Education Accreditation: Fluoride Geochemical Simulation during Water–Rock Interactions under the Effect of Seawater Intrusion

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Abstract: Engineering education is critical for the creation of a more sustainable world, and engineering education accreditation has become the current trend for reform in higher education worldwide. Traditional replication experiment-based teaching cannot meet the standards of engineering education accreditation, and integrating the ideas of engineering education accreditation into experimental teaching is an important aspect of practical teaching. Taking fluoride evolution simulation during water–rock interactions under the effect of seawater intrusion as an example, an exploratory experiment was designed with the idea of engineering education accreditation. The experiment concluded that leached fluoride increases with increasing ratios of seawater and brine water, NaCl levels, and NaHCO₃ levels, but with decreasing CaCl₂ levels, which confirms that seawater intrusion deeply affects fluoride evolution. The saturation index and Fourier Transform Infrared analyses indicate that Ca²⁺ restriction and exchange of F with O–H and Si–O–Si are responsible for fluoride leaching. The experiment was characterized by deeper theory, logicality, and openness, and was also multi-schematic and exploratory. Therefore, it is an ideal subject matter to develop an exploratory experiment. A reasonable teaching link was designed to integrate the ideas of engineering education accreditation. Students were required to creatively and personally devise an experimental design and an expansion to the experiment based on the given databases and other relevant literature and to cooperate and discuss in groups. The experiment not only integrates basic knowledge of water–rock interactions, but also cultivates the awareness of and ability to analyze and solve problems, innovative thinking, scientific literacy, and teamwork. Meanwhile, the experiment effectively supports the graduate requirements of various subjects, including Design/Development Solutions, Research, Applying Modern Tools, Individual and Teams, and Communication.

Keywords: design of exploratory experiment; fluoride leaching; graduation requirements; comprehensive ability; engineering education accreditation; teaching link

1. Introduction

With industrialized civilization, the earth’s resources are consumed in increasingly massive quantities. Incorporating sustainability in processes is an effective solution to this issue, which involves integrating the concepts of environmental protec-
tion, social development, and economic growth into the design, products, and services [1]. Engineering plays a crucial role in shaping our society since it has a profound effect on nature and society, and engineering education is critical for creating a more sustainable world [2].

Economic globalization has promoted the globalization of engineering and higher engineering education [3]. International professional accreditation management systems, which endeavor to make the quality of accredited professional education universally recognized, are gradually being launched. Engineering education accreditation is based on the principles of international substantive equivalence and is an important symbol of education internationalization [4]. Therefore, engineering education accreditation is an important foundation of the international mutual recognition of engineering education and engineer qualifications, and it also serves as an important assurance to improve the quality of engineering education [5–7]. The “Washington Accord”, which is one of the several internationally accredited accords, is well known for its authority and system integrity [4,8,9]. It is widely implemented in many countries worldwide, such as the United States, Britain, Australia, Germany, Ireland, Canada, New Zealand, and Japan [4]. China was enrolled as the 18th formal member of the “Washington Accord” in 2016 [8]. Engineering education accreditation has become a priority in higher education reforms in China and other countries. Engineering education accreditation not only requires the cultivation of students’ basic skills and knowledge, but also emphasizes the cultivation of students’ abilities in engineering practice, professional ethics, social responsibility, leadership negotiation, and self-learning [10–12]. Experimental teaching is an important approach in higher education, and it is also an important way to cultivate students’ practical abilities. However, most of the experimental teachings are based on replication experiments, and students only need to perform the experiments in a systematic way according to the provided instructions [13,14]. Replication experiments emphasize the knowledge of basic theories and skills and the application of various instruments, equipment, and analytical methods [15,16], which is insufficient to meet the needs of engineering education accreditation. Exploratory experiments are centered on students’ subjective initiative [16,17], which not only integrates basic theoretical knowledge into teaching activities but also plays a unique role in cultivating students’ abilities to analyze and solve problems independently, while also promoting scientific literacy, innovative spirit, team awareness, communication, and negotiation. Therefore, designing exploratory experiments using the ideas of engineering education accreditation is an important way to promote the construction of “new engineering” and improve the quality of engineering education [18]. The development of exploratory experiments is an important path for the reform of experimental teachings in higher engineering education.

The water–rock interaction simulation experiment is an important tool for revealing element migration, groundwater quality evolution, rock mechanical properties, and eco-environmental evolution. It has developed rapidly since the 1970s. In the 1980s, the simulation was transformed from a static system into an open system [19]. Water–rock interaction simulation experiment lessons were incorporated into diverse majors such as Engineering Geology, Sedimentary Geology, Paleo-environment, Hydrology and Water Resources Engineering, Environmental Science, and other related majors [19–22]. Based on this, our Hydrology and Environment group considered the typical fluorine evolution during water–rock interactions under the effect of seawater intrusion as an example and established an exploratory experiment integrating the ideas of engineering education accreditation into the experimental teaching process.
In this way, it is expected to provide some reference and experience for the exploratory experiment-based teaching of water–rock interactions.

2. Experiment Design

2.1. Experimental Background

Fluorine is one of the most important bio-elements affecting human health. However, excessive fluoride intake causes typical symptoms of dental fluorosis and skeletal fluorosis and even affects the digestive, endocrine, nervous, immune, and reproductive systems [23]. Among these conditions, drinking water fluorosis is the most common cause of fluorosis worldwide.

In coastal areas around the world, high-fluoride groundwater and fluorosis have been widely documented, such as in the Thoothukudi District of India [24], the east coast of Sri Lanka [25], the Gulf of Thailand [26], Bengal Bay of Bangladesh [26], and Liaodong Bay, Bohai Bay, and Laizhou Bay of China [24,27]. High-fluoride groundwater has become an important factor limiting the safe utilization of groundwater and sustainable development in coastal areas. However, the mechanism underlying the generation of high-fluoride groundwater in coastal areas is unclear.

Seawater intrusion is the most important and unique geological process in coastal areas. There are two types of seawater intrusion as follows: modern seawater intrusion and brine water intrusion. In modern seawater intrusion, modern seawater intrudes freshwater. In brine water intrusion (also called paleo-seawater intrusion), brine water originates from paleo-seawater that was historically detained in sediments because of transgression in coastal areas, and brine water forms as a result of long-term evaporation [27,28].

Seawater (brine water) intrusion significantly changes groundwater’s geochemical properties and possibly accelerates fluorine leaching from rocks (sediments), which may contribute to groundwater fluorine enrichment in coastal areas. The potential reasons for this are as follows: (1) seawater (brine water) intrusion significantly increases the groundwater Na⁺ levels and Na/Ca ratios. The solubility of NaF (41,700 mg/L) is much higher than that of CaF₂ (15 mg/L) [27], and groundwater Na⁺ has a higher affinity for F⁻ than Ca²⁺ and Mg²⁺ [27,29]. Consequently, this process greatly promotes fluorine leaching from the rock (soil). (2) The seawater (brine water) intrusion enriches CO₃²⁻ and HCO₃⁻ in groundwater, and the following reactions are likely to occur under the conditions of Na⁺ and HCO₃⁻ enrichment [30]:

\[
CaF_2 + 2HCO_3^- = CaCO_3 + 2F^- + H_2O + CO_2
\]

or

\[
CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2
\]

These processes potentially intensify the dissolution of insoluble CaF₂ in rock (soil). (3) CaF₂ forms and precipitates because of the strong affinity between F⁻ and Ca²⁺ [27,30,31]. The F⁻ levels in groundwater commonly increase with decreasing Ca²⁺ levels. Seawater (brine water) intrusion causes groundwater to be alkaline, resulting in the precipitation of Ca²⁺ and the enrichment of F⁻ [29]. (4) OH⁻ and F⁻ have the same radii and charges, and can be exchanged with each other [27,32]. The higher pH because of seawater intrusion potentially promotes the exchange of OH in water with F⁻ in the rock (soil), causing more fluoride leaching. (5) The increasing groundwater hardness, TDSs (Total Dissolved Solids), and electrical conductivity because of seawater or brine water intrusion are also conducive to fluoride enrichment in groundwater [27].
Overall, researchers have also indicated that fluoride enrichment in groundwater is closely related to alkaline conditions, with high TDS levels, high Na\(^+\) and low Ca\(^{2+}\) concentrations \cite{27,30,31}, and seawater (brine water) intrusion can cause such changes in the geochemical properties of groundwater. However, seawater intrusion has not been considered when the origin of high-fluoride groundwater in coastal areas is discussed. There are no simulation experiments on fluorine leaching from rocks (soil) under seawater intrusion, and its mechanism remains unclear. Therefore, seawater intrusion and high-fluorine groundwater are highly theoretical and logical, which is a suitable topic for students to independently determine the logical relationships between seawater intrusion and fluorine migration and design experimental schemes. In addition, students can use different solutions to simulate different seawater intrusion conditions by considering different factors. Therefore, the experimental scheme is also characterized by multiformity and openness and has strong exploratory potential. Briefly, this experiment not only integrates the basic theory of water–rock interactions, but also expands the scientific horizon, improves students' ability to analyze and solve problems, and cultivates innovative thinking and scientific literacy. It is an ideal experimental material for the simulation of water–rock interactions. Simultaneously, the teaching process is reasonably designed to promote the construction of “new engineering” and practice the concept of engineering education accreditation by integrating the concepts of engineering education accreditation and advanced technologies to study water–rock interactions into the experiment.

2.2. Experimental Purposes

The following objectives were expected to be achieved through this experiment:

(1) To understand the essential theoretical knowledge of seawater characteristics, the factors influencing groundwater fluoride levels, and fluoride migration laws during water–rock interactions, and to cultivate the consciousness and ability to design exploratory experiments to solve engineering issues based on basic theories.

(2) To master the use of different analysis methods, such as the saturation index (SI) and Fourier Transform Infrared (FTIR) spectroscopy, to explain the element migration during water–rock interactions, and to cultivate the awareness of selecting appropriate modern tools to address engineering issues by comparing their advantages and disadvantages.

(3) To train the abilities of creative thinking, teamwork, consulting-related references, presentations, and communication.

2.3. Experimental Method

Four steps are included in this experimental method, as shown in Figure 1.

(1) Preparation of simulation solution: In this experiment, different proportions of seawater, brine, and freshwater were used to directly simulate different degrees of seawater intrusion that reflect two types of seawater intrusion (modern seawater intrusion and brine water intrusion), and different levels and types of solutions were used to simulate the change in a single factor caused by seawater intrusion. Since there were many influencing factors, the routine experiment only required students to prepare 11 mixtures: freshwater; 1:1 freshwater and seawater; 1:1 freshwater and brine water; pure seawater; pure brine water; and 0.1 mol/L and 1 mol/L NaCl, NaHCO\(_3\), and CaCl\(_2\). Among them, freshwater, 1:1 freshwater and seawater, and pure seawater were used to simulate different intrusion degrees of modern seawater, whereas freshwater, 1:1 freshwater and
Brine water, and pure brine water were used to simulate different degrees of brine water intrusion. The different levels of NaCl, NaHCO₃, and CaCl₂ solutions were designed to simulate the changes in Na⁺, HCO₃⁻, and Ca²⁺ caused by seawater intrusion. The volume of each solution was approximately 2L.

(2) In a batch of experiments, the same rock (soil) samples were used. Approximately 50 g of sample was ground to less than 100 mesh and added to clean 2 L beakers. A 1.2 L volume of each of the 11 prepared solutions was added to different beakers. The beakers were left to stand after stirring for 1 min using a magnetic stirrer. A 150 mL volume of supernatant was taken from each beaker and then centrifuged at 8 h, 16 h, 24 h, 48 h, 96 h, and 192 h to observe the fluoride leaching process over time. Meanwhile, a comparison of fluoride leaching in different solutions at the same time points reveals the differences in fluoride leaching under different conditions. To allow the water and rock to react fully, the beakers were stirred again with a magnetic agitator for 1 min after each sampling and then left to stand. The remaining solution in the beaker was removed using a syringe after the last sampling. The beaker was dried in an oven at 105 °C, and the sample was scraped off with a knife for analysis.

(3) Analysis of fluorine levels in solution: In a series of 50 mL colorimetric tubes, 0.5, 1, 2, 5, 10, and 12 mL of a 1 mg/L fluoride standard solution were added, and the final volume was adjusted to 50 mL using deionized water after a 5 mL volume of ionic strength regulator was added. The potential value was measured using an Intelligent Fluoride Ion Analyzer, and a standard curve was obtained. A 40 mL volume of an experiment sample was transferred into a colorimetric tube. A 5 mL volume of ionic strength regulator was added, and deionized water was added up to a final volume of 50 mL. The potential was measured, and the fluoride level of the solution was calculated according to the standard curve [33].

An Ion Chromatograph (Dionex ICS-90) was used to measure the Ca²⁺ and Mg²⁺ cations in the experimental samples using an IonPac CS12A analysis column and an IonPac CG12A protection column. The eluent used was 20 mmol/L methanesulfonic acid (MSA).

FTIR spectroscopy analysis was performed using a Nicolet 380 Infrared Spectrometer. The KBr lamination method was adopted for this experiment. The rock (soil) sample was first compacted into slices with a diameter of more than 2 cm using a mould and then fixed on the sample table for scanning. The scanning wavelength was 4000–400 cm⁻¹.

(4) Calculation of net leaching of fluorine and other ions: In this experiment, the differences in fluorine levels caused by the different ratios of seawater (brine water) were excluded, and the net leaching amounts were calculated using the following formula: \[ \Delta C_i = C_{i,\text{sample}} - C_{i,\text{initial}} \], where \( \Delta C_i \) represents the net leaching of a certain ion, \( C_{i,\text{sample}} \) represents the level of the ion in the solution, and \( C_{i,\text{initial}} \) represents the ion level in the original solution.

Calculation of saturation index (SI): SI is a thermodynamic index of the solubility of insoluble compounds and is used to discuss the dissolution and precipitation process during water–rock interactions [34]. The calculation formula is SI=\log(IAP/Ksp), where IAP is the ionic activity product and Ksp is the equilibrium constant [34]. In addition, Ksp = γc, where γ is the activity coefficient and c is the ion level. The activity coefficient was calculated according to the Debye–Hückel equation (I < 0.1 mol/L) and the Davies equation (I > 0.1 mol/L). Software Phreeqc 1.1 was used to calculate the SI of CaF₂ in this experiment [35,36].
FTIR spectroscopy data and image processing: Matlab 8.0 software was used to process the FTIR spectroscopy data and generate the figures.

**Figure 1.** The scheme of the simulation experiment.

### 2.4. Main Instruments, Reagents, and Analysis Methods

Main reagents: Seawater, brine water, freshwater, 0.1 mol/L and 1 mol/L NaCl, 0.1 mol/L and 1 mol/L NaHCO₃, 0.1 mol/L and 1 mol/L CaCl₂, 1.0 mg/L fluoride standard solution, ionic strength regulator, and deionized water were used. All the chemicals used were guaranteed reagents (GR) and were prepared by the teacher in advance.

Main instruments and analysis methods: Fluoride levels in solutions were determined using an Intelligent Fluoride Ion Analyzer (BION-1881), together with a PF-1C fluoride-selective electrode; Ca²⁺ levels were analyzed using an ICS-90 ion chromatography instrument; functional groups of soils (rocks) were determined using Fourier Transform Infrared spectroscopy (Thermo Nicolet 380 instrument), with wavenumber ranging from 400 cm⁻¹ to 4000 cm⁻¹; magnetic stirrers, electronic balances, and ovens were used in the simulation experiments. All the analyses were completed in the laboratory of our Experiment Center.

### 3. Experiment Results

#### 3.1. Characteristics of Fluorine Leaching in Different Solutions

In this experiment, soil with a fluoride level of 154 mg/kg was selected as the test material. The seawater was obtained from Jiaodong Bay, Yellow Sea, and the brine water was obtained from Zhenbei Saltern Company. The fluoride levels in the seawater and brine water were 0.82 mg/L and 0.93 mg/L, respectively. Deionized water was used as freshwater with a fluoride level below the limit of detection.

By comparing the differences in fluorine leaching from the soil in different solutions, students can intuitively understand the effect of seawater (brine water) intrusion degrees or a single factor on fluorine evolution during water–rock interactions. As shown in Figure 2, the amounts of leached fluorine from soil were ranked as follows: seawater > 1:1 freshwater and seawater > freshwater; brine water > 1:1 freshwa-
ter and brine water > freshwater. These results intuitively confirm that fluorine leaching from soil increases with increasing proportions of seawater or brine water, which directly reveals the effect of seawater (brine water) intrusion on groundwater fluoride levels [37]. The following conclusions were reached by comparing fluorine leaching in different types of solutions. The leached fluoride amount in 1 mol/L NaCl and NaHCO₃ solutions was greater than that in 0.1 mol/L NaCl and NaHCO₃, indicating that the increased NaCl and NaHCO₃ levels promoted fluorine leaching from the soil. However, the leached fluoride in the 1 mol/L CaCl₂ solution was less than that in the 0.1 mol/L CaCl₂ solution, indicating that the increased CaCl₂ levels restrict fluoride leaching from the soil [37]. CaF₂ is an insoluble compound, and its solubility deeply governs fluoride levels in water [27,31]. Generally, F⁻ and Ca²⁺ levels in water are negatively correlated, and this relationship is observed in a variety of different high-fluoride environments [27,30,32,38,39]. Our observations are also in agreement with previous findings. In brief, high Na⁺ and HCO₃⁻ and low Ca²⁺ conditions are conducive to the fluoride leaching from soil. Through this experiment, students can intuitively understand the factors affecting fluoride leaching during water-rock interactions. In addition, students can personally experience how to design experimental schemes and solve scientific problems based on scientific principles.

3.2. Characteristics of CaF₂ Saturation Index

The SI is an important index reflecting the precipitation and dissolution of minerals during water-rock interactions, and the precipitation and dissolution of CaF₂ is also an important process affecting fluorine evolution during water-rock interactions. As shown in Figure 3, the saturation index of CaF₂ increases with higher proportions of seawater or brine water, implying continuous fluorine leaching from the soil. However, the SI was still less than 0, indicating no saturation or CaF₂ precipitation. The SI values of CaF₂ in 0.1 mol/L and 1 mol/L NaCl and NaHCO₃ were also less than 0, indicating no saturation possibly because of the low Ca²⁺ levels in these solutions. However, the CaF₂ saturation index in the 0.1 mol/L solution was less than 0, whereas that in the 1 mol/L CaCl₂ solution was more than 0, indicating that CaF₂ precipitates.
when the Ca\(^{2+}\) levels increase from 0.1 mol/L to 1 mol/L. Naturally, groundwater fluoride is enriched through mineral dissolution since Ca\(^{2+}\) levels decrease when seawater intrudes [29], which proves that the decrease in Ca\(^{2+}\) levels is an important dynamic in fluorine enrichment in seawater intrusion areas. From this experiment, students can understand the significance of SI in the process of mineral dissolution and precipitation, the analytical role of Phreeqc software in water–rock interactions, as well as the methods of data processing and scientific representation.

3.3. FTIR Spectra Characteristics of Soil

This experiment required students to analyze the mechanism of element migration through the variation in functional groups in the soil during water–rock interactions. Figure 4 illustrates the FTIR spectroscopy characteristics of soil leached using different solutions. The intensities of the O–H vibration peaks at 3400–3500 cm\(^{-1}\) and 1640 cm\(^{-1}\) increased with higher proportions of seawater or brine water, and new O–H vibration peaks appeared at 3241 cm\(^{-1}\) and 3236 cm\(^{-1}\) in the soil samples leached by 1:1 freshwater and brine water, and pure brine water, indicating that the exchange of OH–F was an important dynamic for fluorine leaching when seawater (brine water) intruded. With higher proportions of seawater or brine water, the Si–O–Si absorption peak at 1052 cm\(^{-1}\) was intensified, and the Si–O–Si vibration peak at 460 cm\(^{-1}\) moved toward the lower wavelength direction, indicating that Si–O–Si bonds were also an important group determining fluoride leaching. Additionally, the Si–F stretching vibration peak at 728 cm\(^{-1}\) was weakened with higher proportions of seawater or brine water, which also indicated fluorine leaching. These results are consistent with those of previous studies, which also confirmed that the exchange of F with O–H and Si–O–Si was a common process in fluoride leaching from soil (rock) [40,41].

With an increase in NaCl levels, the absorption peak of the Si–O–Si bonds intensified, but there was no obvious intensification of the O–H bond absorption peak (even a slight weakening). The intensity of the Si–F peak decreased with increasing NaCl levels. With higher NaHCO\(_3\) levels, the absorption peak of Si–O–Si bonds did not change significantly, and the absorption peak of O–H bonds changed significantly, and even a new O–H stretching vibration peak appeared at around 3050 cm\(^{-1}\). Such phenomena indicate that NaHCO\(_3\) affects fluorine migration mainly through
OH–F exchange, whereas NaCl mainly affects fluorine migration in mineral lattices. The peaks at 875 cm$^{-1}$, 1420 cm$^{-1}$, and 1460 cm$^{-1}$ are CO$_3^{2-}$ characteristic peaks [16], which intensified with increasing NaHCO$_3$ levels because of the precipitation of carbonate minerals. However, the intensity of the CO$_3^{2-}$ characteristic peaks decreased with higher NaCl levels, indicating no carbonate mineral precipitation due to low Ca$^{2+}$ levels in the NaCl solutions. The intensity of stretching vibration peaks of Si–F decreased with increasing levels of both NaCl and NaHCO$_3$, indicating fluorine leaching. With higher CaCl$_2$ levels, the vibration peaks of Si–O–Si bonds were obviously weakened and moved toward higher wave numbers. Even the O–H bending vibration peak at 1640 cm$^{-1}$ was intensified. Meanwhile, leached fluoride was observed to decrease with increasing Ca$^{2+}$ levels (Figure 2). These phenomena indicate that O–H and Si–O–Si groups cannot effectively explain the fluorine leaching from soil, and the exchange of F with O–H and Si–O–Si bonds is not the main mechanism of the effect of Ca$^{2+}$ on fluoride leaching from soils. However, the intensity of the CO$_3^{2-}$ characteristic peaks at 875 cm$^{-1}$ and 1460 cm$^{-1}$ increased with higher CaCl$_2$ levels, indicating CaCO$_3$ precipitation because of the high Ca$^{2+}$ levels. This observation is consistent with the above conclusion that CaCl$_2$ affects fluorine leaching mainly through CaF$_2$ saturation (Figure 3). Through FTIR spectroscopy analysis, students can understand the use of modern technologies to analyze the micro-processes of water–rock interactions.
4. Design of Teaching Link

4.1. The Preparation Period Before Class

Our teaching team established four databases guiding students to think deeply about the problem and theory, and students were required to read these databases before class. These databases include the variation characteristics of groundwater properties affected by seawater intrusion (Database 1), factors influencing groundwater fluorine enrichment (Database 2), modern testing and analysis techniques (Database 3), and experimental data-processing techniques (Database 4) (Figure 5). The students were required to summarize the variation in groundwater properties and the potential factors influencing fluorine leaching during water–rock interactions because of seawater intrusion using Databases 1 and 2. Ultimately, students were required to determine which hydrogeological processes of seawater intrusion have a logical relationship with groundwater fluorine enrichment; the aim for students was to independently put forward scientific hypotheses based on the observed phenomena. Database 3 enabled students to understand the various analysis methods for different geochemical properties and compare their advantages and disadvantages. Students were required to select appropriate experimental tools and professional instruments and establish an experimental system to collect data correctly. Database 4 focused on the data-processing technologies involved in this experiment, mainly FTIR spectra interpretation, and Matlab and Phreeqc software applications. Database 4 enabled students to select and use appropriate modern engineering tools to analyze and solve complex engineering problems and understand their limitations. In addition, students were encouraged to refer to other relevant literature. The students were divided into discussion groups and required to write self-study reports before class.

Figure 4. FTIR spectroscopy of soil leached in different solutions.

Figure 5. Database structure and reading requirements.
4.2. Implementation Phase in Class

The teacher mainly explained the following four aspects in class: (1) basic knowledge, including common analysis methods involving geochemical indicators and their comparison, a summary of fluorosis in coastal areas, seawater intrusion, and groundwater geochemical properties, and the factors affecting fluorine leaching during water–rock interactions; (2) FTIR spectra interpretation, and Matlab and Phreeqc software operation and training; (3) an explanation of the experiment including experimental purposes, principles, procedures, aspects requiring attention, etc.; (4) how to perform literature research and write an experiment report. Considering that students have already understood some basic knowledge before the class, self-study and a flipped classroom in groups can be adopted, with students asking questions and teachers answering questions.

The students were divided into several groups and encouraged to optimize the experimental scheme to enhance their understanding and internalization of the basic knowledge and cultivate their scientific research literacy. Considering the teaching hours and experimental workload, this experiment was carried out by “grouping under the guidance of teachers”. The students were divided into three to four groups, and each group was responsible for three to four solutions in the simulation experiment. Each group completed the experimental work independently in batches, which required solidarity, cooperation, and data sharing.

4.3. Expansion of After-School Contents

After class, students were required to independently complete data processing and illustration, analyze and summarize the experimental results, and explore the scientific essence behind the experimental phenomena. To further improve students’ enthusiasm and creativity, students can consult the literature and carry out the following experimental expansion contents:

(1) The routine experiment only simulated the evolution characteristics of fluorine in 11 solutions. Students can analyze the literature and propose other possible factors affecting fluorine leaching from rock (soil) under the condition of seawater intrusion and carry out fluorine leaching simulation experiments using other ratios and types of solutions.

(2) The routine experiment used FTIR spectroscopy and saturation index to explore the relationship between fluorine leaching and active groups, such as O–H and Si–O–Si, and mineral precipitation and dissolution. Based on the literature, students may use other research tools (such as Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy) [21] to explore the relationship between fluorine leaching and other processes (such as complexation or adsorption).

(3) Based on the literature, simulation experiments on the evolution of other elements (such as Cu, Fe, As, etc.) under the effect of seawater intrusion can be designed and performed.

4.4. Score Evaluation

The course score directly reflects the teaching efficiency and learning effect and is also directly related to a series of issues, such as student scholarship evaluation and excellence evaluation. Therefore, reasonable assessment standards should be implemented for experimental teaching. The score evaluation of the experiment should fully consider the comprehensive performance before, during, and after class. The total score should be evaluated according to the proportions of pre-class learning (25%), in-class performance (20%), experimental report (40%), and experimental expansion (15%).
4.5. Effectiveness Evaluation

Exploratory experiments have aroused extensive attention in education because of their roles in cultivating students’ creativity, scientific thinking, and self-learning abilities [16,17], and different exploratory experiments have also been developed. Wang and Lee [42] established an exploratory experiment for a layout design curriculum using a layered-grid approach. Yu et al. [43] designed and practiced exploratory virtual experiments in physics. Endrass et al. [44] presented an exploratory experiment to design a user–character dialog in interactive narratives. “Green” and “Non-green” aspects of noble metal nanoparticle synthesis were introduced using an exploratory laboratory experiment by Sesha et al. [45]. Yao et al. [46] developed an exploratory experiment for an online experiment using the CDIO (Conceive, Design, Implement, and Operate) concept. Wang et al. [47] constructed 48 cases of exploratory experiments for a Digital Electronics Technology course. However, most of these studies mainly focused on the modification of experimental procedures and the new construction of teaching systems based on traditional replication experiments. Zhang et al. [17] also discussed the application of argument-driven inquiry (ADI) in experiment teaching. The designed experiment in this research requires students to independently think over and propose a scheme regarding a complex engineering issue (without validating it), which is a thorough exploratory case. Moreover, the strong theory and logic between seawater and fluoride leaching make it a suitable and effective topic to master the basic knowledge and develop design solutions. Students must independently design their own schemes according to the provided databases and other related literature, and the schemes vary from person to person because the factors considered by each individual vary greatly, which validates the strong openness and in-depth exploratory aspects. This designed experiment mainly focuses on cultivating comprehensive thinking modes and abilities to solve complex engineering issues. Additionally, exploratory experiments are rarely designed based on the ideas of engineering education accreditation. Komives [48] described a laboratory course including an inquiry-based project for ABET (Accreditation Board for Engineering and Technology) accredited engineering programs, which is also based on cookbook experiments and previously published experiments.

The students felt that it was very difficult and even impossible to complete this experiment as undergraduate students when the experiment task was launched because of the lack of related knowledge about seawater intrusion and fluoride evolution and the experience of personally designing an experimental scheme. These students needed a long time to design the schemes before class. However, the students experienced less difficulty during the implementation in class once they completed the consultation of databases and personally designed the scheme before class. Such phenomena imply that they experienced a profound understanding of the basic knowledge and trained their innovative thinking.

Diverse schemes, other than the routine experiments, were designed. For example, most students considered the potential effect of pH on fluoride leaching, and different students used different solutions, such as KOH, NaOH, NH₄OH, and HCl, etc. Additionally, the effects of salinity, organic carbon, and microorganisms were also studied. Some groups even used solutions with different Na/Ca ratios for the simulation. Consequently, the experimental reports varied from one student to another because of the multiple schemes and the open and exploratory aspects.

The students showed great enthusiasm and initiative in experimental implementation, group discussion, and communication. Most students desired to carry out the expansion experiments they designed during their spare time. Some projects were
even applied based on these experiments, such as the College Students’ Innovative Entrepreneurial Training Plan Program.

5. Supporting Graduation Requirements for Engineering Education Accreditation

The key to engineering education accreditation is to support graduation requirements through the curriculum. The graduation requirements for engineering education accreditation in China include 12 general standards: Engineering Knowledge, Analysis of Issues, Design/Development Solutions, Research, Applying Modern Tools, Engineering and Society, Environment and Sustainable Development, Professional Norms, Individuals and Teams, Communication, Project Management, and Life–long Learning [10,49]. This experiment mainly supports the following graduation requirements.

Design/Development Solutions: Although high-fluorine groundwater is universal in coastal areas, there is still no conclusive conclusion regarding its causes. This experiment requires students to apply the basic principles of relevant disciplines and understand the logical relationship between seawater intrusion and fluorine leaching during water–rock interactions. Students should independently design innovative experimental schemes for fluoride evolution simulations by considering various factors affecting fluorine leaching. The experiment is exploratory and open. This experiment can guide students to develop and design reasonable solutions to solve complex engineering problems using the basic principles and methods of the subject.

Research: This experiment requires students to independently propose a simulation experiment scheme considering factors influencing high-fluoride groundwater, and the suitability of the research methods and the relevant materials. Reasonable analytical instruments and research methods are selected to collect data correctly. Based on the data analysis, reasonable conclusions are drawn for the cause of high-fluorine groundwater in coastal areas. A research chain of “problem raising–scheme design–data collection–conclusion analysis” is formed, with students participating in the whole process. This experiment trains students to conduct research on complex engineering problems based on scientific principles and methods, including designing experiments, analyzing and interpreting data, and obtaining reasonable and effective conclusions using information synthesis.

Applying Modern Tools: This experiment requires students to learn the modern analysis methods and techniques for the geochemical properties measured in the experiment, such as the ion selective electrode method, fluorine reagent spectrophotometry, fluorescence analysis, atomic absorption spectrometry, ion chromatography, high–performance liquid chromatography, and the thorium nitrate titration method for fluorine determination [50,51]. The advantages and disadvantages of each method are analyzed, and the appropriate tools and techniques are chosen to solve the problem. This experiment is conducive to cultivating students’ consciousness and ability to choose and use the appropriate technology, modern engineering tools, and information technology tools to solve complex engineering problems.

Individuals and Teams: Group discussion is adopted, and the data are commonly shared in this experiment, which requires effective communication and cooperation. In cooperative projects, one can play the role of both a leader and a team member. This experiment prepares students to assume the role of an individual, team member, and leader in a multidisciplinary team setting.

Communication: In this experiment, students are required to independently consult and read the relevant literature, understand development trends, research hot spots, and summarize the variation in groundwater properties caused by seawater intrusion and its relationship with fluorine leaching during water–rock interactions.
Students should make clear statements in class and communicate with their classmates and teachers. This experiment can develop students' ability to effectively communicate with industry peers and the public on complex engineering issues, including writing reports, designing documents, presenting speeches, clearly expressing or responding to instructions, etc.

6. Conclusions

Engineering education accreditation is an important route to achieving international mutual recognition of engineering education and guarantees the improvement of the quality of engineering education around the world. Traditional replication experiments cannot meet the standards of engineering education accreditation, and an exploratory experiment simulating fluorine evolution during water–rock interactions caused by seawater intrusion was designed to integrate the ideas of engineering education accreditation. The experiment confirmed that fluoride leaching from rock (soil) was promoted by higher ratios of seawater or brine water, NaCl levels and NaHCO₃ levels, and weakened with higher CaCl₂ levels, which directly revealed the effect of seawater intrusion on fluoride geochemical evolution. An analysis of the SI and FTIR spectroscopy indicated that Ca²⁺ restriction and exchange of F with Si–O–Si and O–H govern fluoride leaching. The experiment has the unique advantages of deeper theory, strong logicality, multiple potential schemes, and open and exploratory aspects to act as an exploratory experiment. Four databases were established, and a reasonable teaching link was designed considering the ideas of engineering education accreditation. The experiment not only requires students to master the basic theories and methods of water–rock interactions, but also it arouses the students’ subjective initiative and cultivates independent analysis and problem-solving, innovative thinking, scientific literacy, and teamwork consciousness. This designed experiment strongly supports the graduation requirements of “Design/Development Solutions”, “Research”, “Applying Modern Tools”, “Individuals and Teams”, and “Communication” for engineering education accreditation, which achieves a deep integration of exploratory experiments and the engineering education accreditation concept and provides some experience and reference to develop other exploratory experiments integrating the ideas of engineering education accreditation.

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References


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