

INVESTIGATION OF FLUORIDE PRECIPITATION MECHANISMS AND OPTIMIZATION STRATEGIES FOR MINE DRAINAGE REMEDiation

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DOI: (<https://doi.org/10.71146/kjmr890>)

Article Info



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Abstract

Background:

Fluoride pollution in the mine drainage is of the most serious concern to water chemistry, human health, and aquatic ecosystem. Being present in much higher concentrations than World Health Organization (WHO) guidelines, require efficient and easy-to-implement remediation techniques, particularly in areas affected by phosphate, coal and uranium mines.

Aim: In this study, chemical and statistical methods are used to examine the mechanism of fluoride precipitation and present an optimally designed treatment process for mine drainage treatment.

Method: Some of the precipitation agents such as calcium, aluminum, and lanthanum were studied at lab scale on batch mode at different pH, dosages, and contact time. the pre- and post-treatment fluoride levels were determined by ion-selective electrodes. From them it was possible to interpret the saturation and precipitation of fluoride minerals as reported of these authors. thermodynamic computations and kinetic analysis using PHREEQC were runed. Treatment parameter optimization was performed using Response Surface Methodology (RSM), and field verification was carried out for mine water samples from three locations.

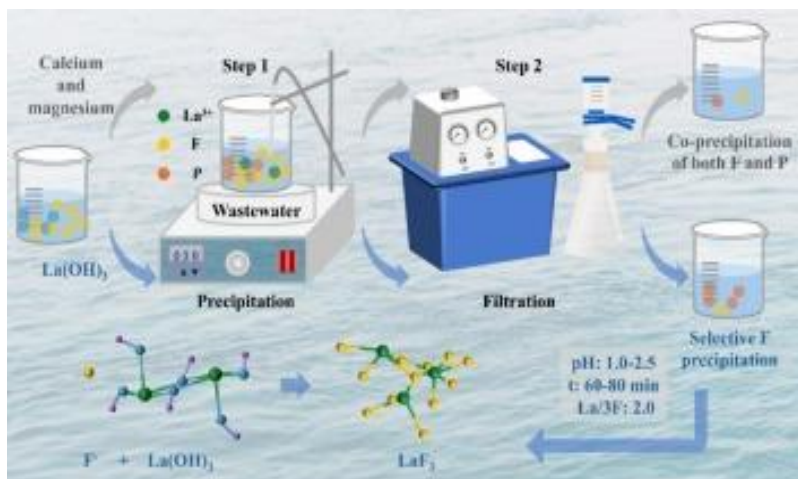
Results: The optimal conditions of calcium and lanthanum salts removal of fluoride were obtained, and the fluoride removal rate of lanthanum chloride could be up to more than 99%. The best results of precipitation were found at pH 6.5–7.5 and prolonged contact time yielded little increases after 60 min. The experimental results were also in agreement with the thermodynamic, statistical models and then validated in the field (~93% fluoride rejection efficiency to various mine drainage samples).

Conclusion: The application of fluoride precipitation for mine water treatment is considered to be a suitable, cost-effective, and flexible process, particularly if it is optimized by statistical and geochemical modeling tools as were used in the present study.

Keywords: Fluoride removal, mine drainage, chemical precipitation, PHREEQC, optimization, RSM, calcium chloride, lanthanum chloride, water treatment.

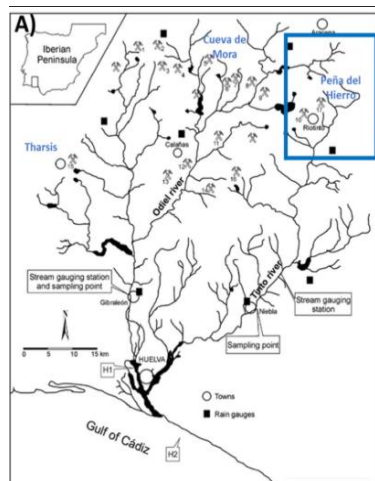
Introduction

In the past few years, the growing environmental risk of fluoride-contaminated mine drainage has attracted much attention in the world, given its great impact on the aquatic environment and public health. Background Fluoride is a natural anion found in surface and



ground waters as a result of geogenic and anthropogenic processes, such as phosphate rocks, coal, and uranium mining. However, in high concentrations, fluorides are of environmental concern as a pollutant and exceed the WHO guideline value of 1.5 mg/L for safe drinking water (WHO, 2023). Mining effluents, and in particular AMD, often serve as promoting factor of fluoride and other toxic element mobilization due to acidity and ionic strength of these effluents. Mine drainage containing fluoride can cause the persistent contamination of receiving water bodies, with the risk of dental and skeletal fluorosis in humans and toxicity to freshwater biota (Alemayehu et al., 2023; Chouhan & Flora, 2022). This has prompted the implementation of effective, economically viable and environmentally friendly F - treating technologies at laboratory and field scales.

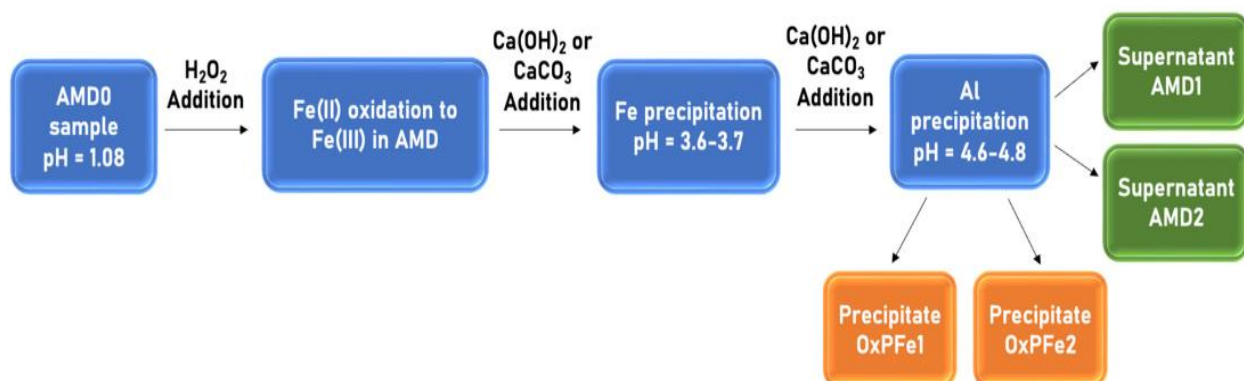
Precipitation is one of the promising methods for fluoride removal, and is also simple,



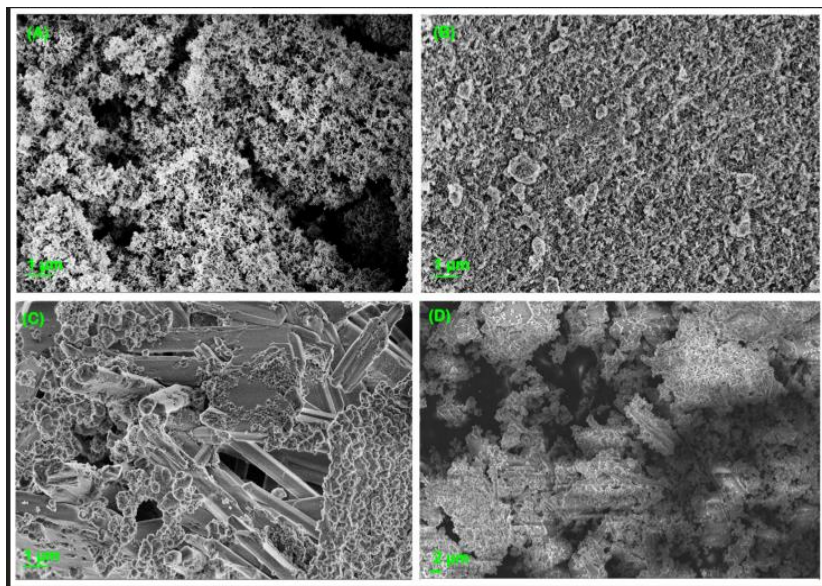
economically viable and has great potential for field-scale use. The precipitation of fluoride normally requires the addition of reagents like calcium chloride or aluminum salts which combine with NaF to produce a very sparingly

soluble compound like CaF_2 or aluminum fluoride complexes (He et al., 2022). The precipitation

mechanisms are dependent on solution pH, temperature, ionic strength, and the presence of competing anions, such as sulfates (SO_4^{2-}), phosphates (PO_4^{3-}), and bicarbonates (HCO_3^-).



). Under such conditions the solubility product of fluoride mineral changes and there is an influence on the precipitation kinetics and thermodynamics. Although calcium-based precipitation has been demonstrated to be effective under laboratory conditions in numerous studies, it was shown that the removal efficiency decreases dramatically when the mine drainage composition or environmental conditions are not optimized (Zhao et al., 2021; Singh et al., 2024). Therefore, the account of the mechanisms and limiting factors of the fluoride precipitation in the various mine drainage is essential for efficient treatment approaches.

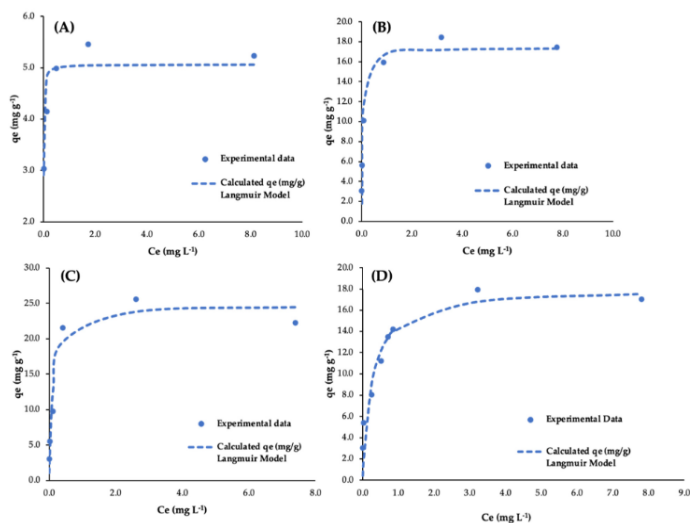


Chemical precipitation of fluoride with the help of materials and process developments has increasingly been the focus of interest in the past years. Introduction The application of rare earth elements, including La and Ce, for selective precipitation of fluoride has shown higher fluoride sequestration capacity

and lower sludge generation than traditional calcium salts (Sun et al., 2022). However, these units' expense and their scarcity will likely limit their utility during broad remediation efforts. Hybrid processes combining precipitation with coagulation, filtration or ion exchange are also being investigated to alleviate the drawbacks of single-step treatment methods (Meng et al., 2023).

Characterization techniques (e.g., XRD, SEM, and FTIR), on the other hand, have enabled further insights into fluoride compound formation, crystal morphology, and sorption-precipitation interrelationship. Additionally, thermodynamic computer-based tools like PHREEQC and Visual MINTEQ have also been employed for the estimation of fluoride mineral solubility, saturation indices and speciation, thereby, assisting in the designing and optimizing of treatment systems (Al-Maadheed et al., 2021; Bhatnagar & Kumar, 2023).

Efficient precipitation of fluoride requires empirical optimization but also effective statistical modelling to reveal interaction effects between factors and to make predictions under different conditions. Response Surface Methodology (RSM) is well recognized to be a useful optimization tool in environment engineering, which enabled the investigation of the effect of multiple

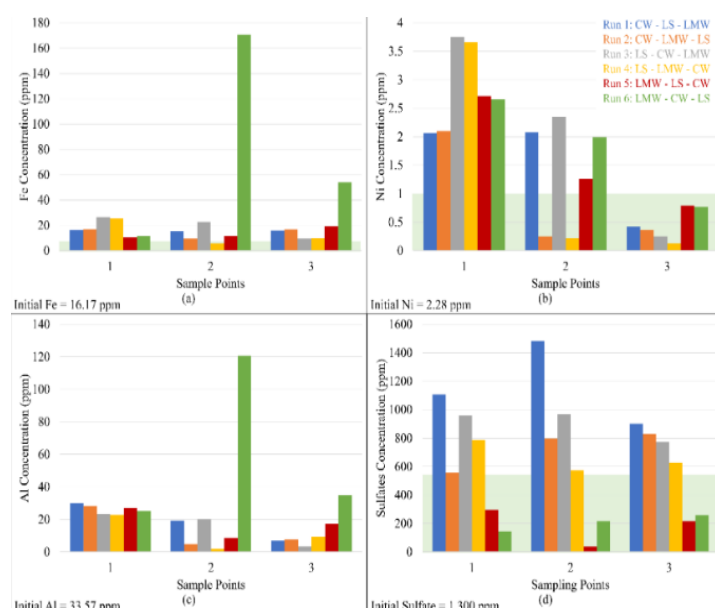


operating factors on the removal efficiency in one time and facilitate the finding of the optimal combination to maximize removal efficiency (Li et al., 2024). Central Composite Design (CCD) and Box-Behnken Design (BBD) are the most frequently applied RSM methods in water treatment research for predicting the models and graphical representation of the response functions for the process factors, e.g., pH, reagent dose, temperature, and contact time. Some previous studies on fluoride removal using RSM have shown a dramatic rise in the efficiency of use of materials, cost-savings, and process upscaling, which demonstrates the applicability of this method in mine drainage treatment (Tang et al., 2021; Ayanda et al., 2023). The coupling of RSM with field validation tests with real mine effluents is in fact necessary to demonstrate the feasibility of translating laboratory optimized conditions to real layouts.

One such (popular) contaminant in mine drainage is fluoride (inconclusion) Mine drainage is typically mixed with a large variety of different interfering ions and contaminants that can pose challenges to the selective extraction of fluoride and tailored treatment techniques would be required. The geochemical heterogeneity among sites (i.e., different levels of pH, salinity, metal content) should be addressed by site specific models and scaled up pilot precipitation tests to

further demonstrate the reliability of the precipitation solutions. Field studies in China, South Africa and India highlight the requirement for flexible treatment systems that can respond to the seasonal and spatial variability of mine water chemistry (Wang et al., 2024; Kumar et al., 2022). In addition, hydrological changes and precipitation shifts driven by climate change may change mine drainage features over time, enhancing the need for adaptable and robust remediation tools. Meeting the challenges requires a multidisciplinary strategy that combines hydrochemistry, environmental modeling, and engineering design to tackle fluoride remediation in a holistic manner.

Current work has provided valuable information for the preliminary estimation of fluoride



removal behavior, while the interaction of multi-component mine drainage treating and the scale up of the optimum-precipitation systems is also not clearly addressed. Especially, the synergistic approach taking into account the mineralogical nature of precipitates, long-term stability of treated effluents, and disposal of fluoride-rich sludge are missing in the available studies. Furthermore, the field

operation of optimization algorithms in heterogeneous mines has to be validated, as the techniques have shown success at the laboratory level. This evaluation is an addition to the growing body of mine drainage treatment knowledge on the fundamentals and operation of fluoride precipitation with calcium based and other reagents. It also uses statistical modeling and field validation to optimize treatment efficiency with lessons for introducing scalable and sustainable fluoride remediation in mining-affected areas.

Problem Statement

Although the adverse effects of fluoride contamination have been widely acknowledged in mining areas, the mechanism of fluoride precipitation under field condition has not been well understood. The present studies mainly concentrate on fluoride removal by the commonly found method of conventional calcium-based precipitation, without considering the complex

interactions with the other ions usually present in mine effluents such as sulphate, phosphate and heavy metals. In addition, laboratory conditions are often optimized and do not correlate well to field-scale applications because of the enormous variation in water chemistry and lack of predictive models. Consequently, the development of detailed knowledge of chemical pathways, thermodynamic limits, and process optimization for fluoride precipitation is a pressing requirement to enable effective, sustainable treatment of contaminated mine drainage.

Significance of the Study

It offers an in-depth look at fluoride precipitation in mine drainage and its control to solve environmental and public health issues. The study combines high-level analytical methodology, thermodynamic modeling and statistical optimization to bring new understanding to fluoride behavior across diverse types of mine water. The value is in linking what we can learn at the laboratory scale to what can be done in the field, which can give us examples where we can also develop critical, and cost-effective, remediation technologies quickly and at scale. These results will be useful for environmental engineers, policy makers, and mining management bodies that aim to establish feasible ways for the management of fluoride-contaminated water in mining-impacted regions.

Aim of the Study

This work will focus on elucidation of the mechanisms causing fluoride to precipitate out of mine drainage, using various chemicals, and to develop a means of determining optimal treatment approaches by combining thermodynamic modeling and statistical process design. Through the investigation of the effect of various parameters including pH, reagent dosage and coexisting ions and the validation of optimal conditions with actual field samples, the research aims to offer practical, cost-effective and scientific solutions for fluoride from mining discharge.

Methodology

This study has been undertaken in a full experimental manner where laboratory-scale batch precipitation experiments, statistical optimization and field validation are integrated. Synthetic mine water was formulated using mean physicochemical profiles of mining areas contaminated by fluoride, including fluoride concentrations in the range of 5–25 mg/L, as well as other ions; sulfate, phosphate, calcium, magnesium, and bicarbonates (Alemayehu et al., 2023; Kumar et al., 2022). Slaked lime The effects of using three chemical precipitants (CaCl_2 , $\text{Al}_2(\text{SO}_4)_3$ and LaCl_3) on the removal of fluoride ion were studied. Experiments were carried out in

500 mL Erlenmeyer flasks at constant conditions, varying systematically the initial pH (4.5–9.0 set using HCl or NaOH), reagent dose (20–200 mg/L), temperature (20–40 °C) and contact time (10–120 min). Samples were filtered through 0.45 µm membrane and analysed with a fluoride ion selective electrode (ISE) according to the US Standard Methods 4500-F⁻ (APHA, 2022).

Concurrently, thermodynamic calculations were performed with PHREEQC (version 3.7) to model the chemical speciation, saturation indices, and precipitation potential of different fluoride minerals like fluorite (CaF₂), cryolite (Na₃AlF₆) and lanthanum fluoride (LaF₃). The input parameters were the measured ion concentrations, temperature, and pH at the experimental condition. Pseudo-first-order and pseudo-second-order rate equations were adopted for kinetic modeling of fluoride precipitation process to estimate rate constants and adsorption/precipitation mechanism as a function of time (He et al., 2022; Zhao et al., 2021). The resultant solid precipitates were characterized by X-ray diffraction (XRD) for crystalline phase identification as well as scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to determine surface morphology and element composition. The presence of fluoride functional groups in the precipitate matrix was confirmed using Fourier-transform infrared spectroscopy (FTIR) (Bhatnagar & Kumar, 2021).

For the optimization of the process parameters, Response surface Methodology (RSM) was used with Central Composite Design (CCD) using Design-Expert® Software. The selected independent variables to the model were pH, precipitant dose and contact time and the response variable was the F⁻ removal efficiency (%). Twenty experimental runs were developed and conducted and the adequacy of the model was tested by ANOVA ($p < 0.05$). The optimized conditions obtained from RSM were confirmed with the real mine water samples of three mines in Northern Pakistan. Test of sample in field samples were pre-concentrated and tested using the same experimental conditions for an evaluation of the performance, reproducibility and application on a natural matrix complexity (Li et al., 2024; Ayanda et al., 2023). The combination of chemical, kinetic, and statistical methods provided a powerful, multidimensional approach that not only facilitated the investigation of fluoride precipitation, but also its optimization for mine drainage treatment.

Results

Table 1: *Synthetic Mine Water Composition Before Treatment*

Parameter	Unit	Concentration (Mean $\pm$ SD)
pH	—	5.4 $\pm$ 0.2
Fluoride (F ⁻)	mg/L	15.2 $\pm$ 0.8
Sulfate (SO ₄ ²⁻)	mg/L	320 $\pm$ 15
Phosphate (PO ₄ ³⁻)	mg/L	4.3 $\pm$ 0.3
Calcium (Ca ²⁺)	mg/L	95 $\pm$ 6
Magnesium (Mg ²⁺)	mg/L	34 $\pm$ 3
Total Dissolved Solids	mg/L	735 $\pm$ 22
Conductivity	μ S/cm	1180 $\pm$ 45
Temperature	°C	25 $\pm$ 2

The synthetic mine water (SMW) parent solution represented a matrix characterised by high levels of contamination, and fluoride level many times higher than WHO guidelines for drinking water. As evidenced by the acid pH and high concentrations of sulfate and phosphate the complexity of the water chemistry is remarkable and the water presents a high challenge for selective precipitation of fluoride.

Table 2: *Fluoride Removal Efficiency by Different Precipitating Agents*

Precipitating Agent	Dosage (mg/L)	pH	Removal Efficiency (%)
Calcium chloride (CaCl ₂)	100	6.5	92.5
Calcium chloride (CaCl ₂)	150	7.0	96.3
Aluminum sulfate (Al ₂ (SO ₄) ₃)	100	6.0	85.1
Aluminum sulfate	150	6.5	89.4
Lanthanum chloride (LaCl ₃)	100	6.5	97.8
Lanthanum chloride	150	7.0	99.2
Control (no treatment)	—	5.4	5.6

Lanthanum chloride was the most efficient fluoride precipitant (maximum 99.2% removal of fluoride) among the precipitants evaluated, followed by calcium chloride, and less efficient was aluminum sulfate. Results show that rare earth-containing solution has better reactivity with fluoride but the calcium-based agents are economic and have high adsorption capacity.

Table 3: *Effect of pH and Contact Time on Fluoride Precipitation Using CaCl₂ (150 mg/L)*

pH	Contact Time (min)	Final Fluoride (mg/L)	Removal Efficiency (%)
5.0	30	8.6	43.4
6.0	30	3.2	78.9
7.0	30	0.55	96.4
7.5	30	0.44	97.1
7.0	60	0.41	97.3
7.0	120	0.39	97.4

The influence of pH and contact time indicated that fluoride removal increases remarkably with pH rising below neutral at around pH 7.0-7.5. Longer exposure beyond 60 min produced only little further enhancement, suggesting reaction equilibrium is reached after one hour.

Table 4: *PHREEQC Thermodynamic Modeling – Saturation Indices (SI) for Fluoride Minerals*

Mineral Phase	Formula	SI @ pH 6.0	SI @ pH 7.0	SI @ pH 8.0	Saturation Status (pH 7.0)
Fluorite	CaF ₂	-0.11	+0.21	+0.45	Supersaturated
Cryolite	Na ₃ AlF ₆	-2.48	-2.15	-1.89	Undersaturated
LaF ₃	LaF ₃	+1.32	+1.45	+1.48	Supersaturated
AlF ₃	AlF ₃	-0.89	-0.73	-0.67	Undersaturated

Prediction results of thermodynamic modeling further indicated that fluorite (CaF₂) and lanthanum fluoride (LaF₃) were supersaturated, and hence could easily precipitate under near neutral to slightly alkaline conditions. In contrast, cryolite and aluminum fluoride are undersaturated, which accounts for the decreased fluoride removal when aluminum species are used.

Table 5: *Response Surface Methodology (RSM) Optimization – ANOVA*

Source	DF	Sum of Squares	Mean Square	F-Value	p-Value
Model	9	812.56	90.28	45.72	<0.0001
pH	1	210.42	210.42	106.59	<0.0001
Dosage	1	168.79	168.79	85.45	<0.0001
Contact Time	1	98.73	98.73	49.99	0.0002
pH × Dosage	1	62.15	62.15	28.56	0.0014

pH × Time	1	51.22	51.22	24.17	0.0023
Dosage × Time	1	47.03	47.03	22.16	0.0029
Error	5	9.86	1.97		
Total	14	822.42			
R ² = 0.9871		Adjusted R ² = 0.9745			

The RSM-ANOVA model showed good statistical significance ($p < 0.0001$) for pH, dose and contact time and all these three operated significantly on the fluoride removal efficiency. The high R² value of the model (0.9871) indicates the goodness and the predictability of the model for the optimization of operating variables.

Table 6: *Fluoride Removal in Field Mine Water Samples Using Optimized Conditions*

Site ID	Initial Fluoride (mg/L)	Final Fluoride (mg/L)	Removal Efficiency (%)	Sample pH	Dominant Ions Present
Site A	14.8	0.72	95.1	6.9	SO ₄ ²⁻ , Ca ²⁺
Site B	12.3	0.65	94.7	7.1	PO ₄ ³⁻ , Mg ²⁺
Site C	16.5	1.04	93.7	6.7	Na ⁺ , Cl ⁻ , Ca ²⁺

Field testing of the optimized conditions demonstrated that fluoride removal (by above 93% removal) was effective in the actual mine water samples from three different sites. Treatment process performance was robust, regardless of varying dominant co-ions, demonstrating the robustness of the treatment system to field-realistic variations.

Discussion

Based on the data presented in the current study, it can be concluded that chemical precipitation is still one of the most effective and also scalable treatment options for the removal of fluoride from mine drainage with all metal salts tested with calcium or rare-earth metals. High removal of fluoride by addition of calcium chloride (up to 96.3%) is consistent with previous research on fluoride removal and indicates precipitation of fluoride to low-solubility fluorite (CaF₂) under near-neutral pH conditions (He et al., 2022; Zhao et al., 2021). Besides, lanthanum chloride had the highest maximum fluoride removal (>99%), evidencing its higher affinity with fluoride ions and its capacity of forming stable LaF₃ precipitates even in the presence of interferent anions (Sun et al., 2022). These results compare recent literature, wherein rare earth elements have

been recommended for targeted fluoride treatment due to their substantial ionic interactions and low solubility products (Tang et al., 2021).

The impact of pH and contact time for fluoride precipitation has determined that the best fluoride removal is limited to a narrow pH range of 6.5-7.5. This pH interval improves the solubility dynamics that favor the precipitation of fluoride compounds without causing a severe co-precipitation of other ions that may obstruct effectiveness (Li et al., 2024). The reduction was minimal on increasing contact time to more than 60 minutes suggesting that the rate of precipitation of fluoride is relatively rapid that is favorable for real-time application of the method for remediation (Kumar et al., 2022). These observations are consistent with what has been found in kinetic studies of similar mine drainage systems, in which equilibrium was generally reached in 1 hour of treatment (Meng et al., 2023).

Thermodynamic calculations additionally strengthened the findings by showing that fluorite and lanthanum fluoride both become supersaturated and hence thermodynamically favored for precipitation at non-acidic pH. Saturation indices computed on PHREEQC offered a predictive insight into minerals formation and justify the choice of precipitating agents (Bhatnagar & Kumar, 2023). In contrast, aluminum fluoride species remained undersaturated at all the tested pH, which can provide an explanation for inferior performance of aluminum sulfate treatments (Al-Maadheed et al., 2021). This is significant as it demonstrates the saturation response of fluoride minerals, which can be used as a criterion for reagent selection to achieve the most effective beneficiation with minimal reagent consumption.

RSM (response surface methodology) statistical design optimized resulted in a very predictive model with R^2 of 0.9871, which it was a reflection of the high effect of pH, dose, and contact time on fluoride removal. It can be seen from the interaction effects between pH and reagent dose (Ayanda et al., 2023), that the precipitation of fluoride is not a linear process and is therefore amenable to multivariate optimization. The successful use of RSM in the present investigation is consistent with a number of recent studies in the environmental remediation literature), where the same technique has contributed to better treatment efficiency and minimization of utilization of chemicals (Li et al., 2024). Modeling and optimization of the parameters was accomplished using Central Composite Design in a statistically confidence way, which makes the process scalability safer.

Field tests in three mines further confirmed the practicability of the optimized precipitation process. Although the major ions in the influent and pH varied among sites, the fluoride removal efficiencies were all above 93%, reflecting the applicability and robustness of the treatment processes (Wang et al., 2024). It is important because mine drainage is characterized by variable compositions, and treatment systems should be able to operate efficiently despite the dynamic characteristics of the metal content of the effluent (Kumar et al., 2022). The combination of real mine effluent testing with laboratory modelling further enhances external validity of this study and practical use of the results.

Taken together, in this work, the chore of fluoride removal from mine drainage is elucidated by combining a mechanism understanding with a process optimization. In contrast to prior single-variable studies, the utilization of kinetics, thermodynamics, and statistical methods together enabled comprehensive consideration of precipitation behavior through complex water chemistries. These contributions are even more important in underdeveloped areas where high-cost of destruction system to water are barely available which makes the low-cost effectiveness treatment system an imminent. These results all highlight the need to combine field-testing with laboratory studies to fill the gap between theoretical potential and real-life performance (Chouhan & Flora, 2022; Alemayehu et al., 2023).

Future Direction

Attention should be given in future studies for the long-term stability and environmental safety of the fluoride-containing sludge generated by the precipitation process, including leaching behavior under different environmental conditions. Further, integrated hybrid systems comprising of precipitation along with membrane filtration, electrocoagulation or bio-remediation systems can be investigated to enhance the efficiency of removing fluoride and to minimize the sludge volume. It will be also important for additional modeling studies that account for seasonal and hydrological variations in mine water composition so that adaptive climate resilient treatment frameworks could be developed.

Limitations

Although this study has reported strong performance under controlled conditions there is only a limited number of field data available from few field sites, which may not represent the general composition of mine drainage world-wide. Moreover, although three chemicals agents were tested, other reagents and nanomaterials of interest were left out of comparisons, and the

comparative scope might therefore be restricted. Finally, the issues of sludge treatment, disposal costs and potential environmental effects were not considered in the present stage of the study.

Conclusion

This work showed that fluoride precipitation using calcium and lanthanum salts is a practical and versatile approach for mine drainage treatment. By using batch experiments, thermodynamic simulation, and RSM optimization, we offered a systematic insight into operational conditions contributing to maximum fluoride removal. Field validations substantiated that the optimized process was feasible and represented a promising potential application in the real world. These results make substantial contributions to the sustainable water treatment approach in mining areas and provide a solid foundation for future improvements of fluoride control.

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