

LABORATORY TESTS ON THE OCCURRENCE OF FLUORIDE RICH GROUNDWATER OF TONO AREA, JAPAN

Abdelrahman M. ABDELGAWAD¹, Kunio WATANABE² and Shinji TAKEUCHI³

¹Geosphere Research Institute, Saitama University (255 Shimo-Okubo, Sakura-ku, Saitama, 338-8570 Japan)

²Geosphere Research Institute, Saitama University, Professor, (255 Shimo-Okubo, Sakura-ku, Saitama, 338-8570 Japan)

³Tono Geoscience Center, Japan Atomic Energy Agency, (1-64, Yamanouchi, Akeyo, Mizunami, Gifu, 509-6132 Japan)

High concentration of fluoride ion up to 12 mg/l is observed in deep groundwater at the Tono area, Japan. A simple but general method to evaluate the occurrence of high fluoride ion concentration in groundwater has reported in this study. Our method based on the water-rock interaction test using different sizes of granite powders sampled from a boring core drilled at the site. Results indicated that, the weathering of granitic rock might be one of the key components for changing the fluoride ion concentrations. And also the increase of the reaction time led to enhance leaching of the fluoride ion from granite.

To deduce the contribution of the co-existence of the chemical parameters, which affected on the change in the fluoride ion concentration, a stochastic model was developed. This model shows significant evaluation of the water-rock interaction test with the chemical data of a low Na-(Ca)-Cl water-type. Results from our stochastic model indicated that the approximation reaction time of the water-rock in the granitic groundwater was about 300 days at this region.

Key Words: groundwater, fluoride, water-rock interaction, stochastic model, granite.

1. INTRODUCTION

Concentration of fluoride ions in groundwater that is higher than the Japanese environmental standard (0.8 mg/l) is found in the Tono area, central Japan^{1), 2)}. There is a growing demand to develop methods for recognition sources of these species. It was observed that fluoride ion concentration was mainly varied according to the depth of the groundwater^{1), 2)}. This variation could be due to the occurrence of different chemical reaction processes, the change in structural and textural properties of different types of rocks or the mixing process among the different types of groundwater³⁾.

Iwatsuki et al.²⁾ constructed a hydrochemical conceptual model in which they have described groundwater chemistry and chemical evolution processes around the site of the Mizunami underground research laboratory (MIU site), Tono, Japan. Iwatsuki's model exhibited that the groundwater mainly divided into three types. The first was the Na-Ca-HCO₃ type of water that evolved

in the Akeyo and Hongo formations (sedimentary rocks overlaying granite basement). The second and third types were the groundwater in the Toki-lignite and the Toki granite. In both types, a mixture of higher and lower salinity water (Na-(Ca)-Cl water-type) was observed.

The main objective of this study is to evaluate the occurrence of high concentration of fluoride ions in groundwater of the area around MIU site, as well as to deduce the influence of the reaction time and the co-existence of chemical components on the leaching of fluoride ion from granitic rock. In this current study, sets of water-rock interaction tests were carried out in a laboratory of Geosphere Research Institute Saitama University (GRIS). Based on our experimental results, a stochastic empirical model was developed for the simulation of the chemical compositions in the groundwater. Also it is a preliminary study to estimate the reaction time of the groundwater. The release time of the fluoride ions from granitic rock shows significant influence in the area around MIU site.

The findings in this study may be enhance the conceptual understanding of the key chemical parameters that might control the dissolution activity of fluoride ion in the groundwater.

2. STUDY AREA

(1) Characteristics of the MIU Project

The MIU research project has been conducted by Japan Atomic Energy Agency (JAEA) at the MIU site, Tono area, central Japan to establish techniques for investigation, analysis and assessment of deep hydrogeological environment. The site is mainly composed of two 1,000 m shafts (the Main and the Ventilation Shafts) and branch tunnels at research levels. Before the MIU construction, shallow boreholes (MSB-1, 2, 3 and 4) and a deep borehole (MIZ-1) were drilled in the site for construction of the conceptual hydrogeological model and the numerical groundwater flow simulation model. Another two boreholes (DH-2 and 15) were drilled around the MIU construction site⁴⁾. The locations of boreholes in MIU site were illustrated in **Fig. 1**.

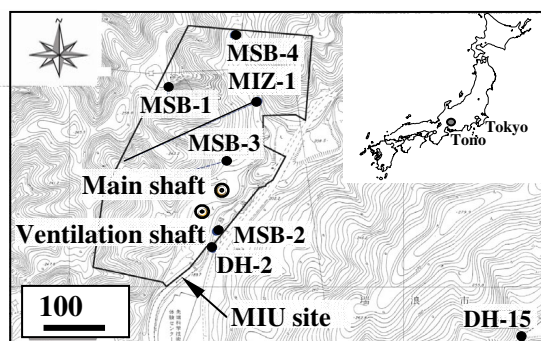


Fig. 1 MIU construction site and boreholes locations.

(2) Geology and hydrochemistry of Tono area

In Tono area, Tertiary sedimentary rocks, namely, Mizunami Group (composed of the Hongo, Akeyo and Toki-lignite bearing formations) unconformably overlying the Cretaceous granite (Toki granite). Toki granite is structurally divided into two types, namely, upper highly fracture domain and lower sparsely fracture domain. A thin layer in the upper part of Toki granite is highly weathered. The major minerals forming Toki granite are Quartz, feldspar, K-feldspar and biotite, associated with accessory minerals such as pyrite, ilmenite and zircon¹⁾.

The hydrochemical conceptual model shows that the Na-(Ca)-Cl water-type in granitic rock can be subdivided into two types. The groundwater shallower than approximately -400 masl (meter above sea level) is considered as low Na-(Ca)-Cl water-type. The deep part of granite is dominated by a high Na-(Ca)-Cl water-type, as schematically

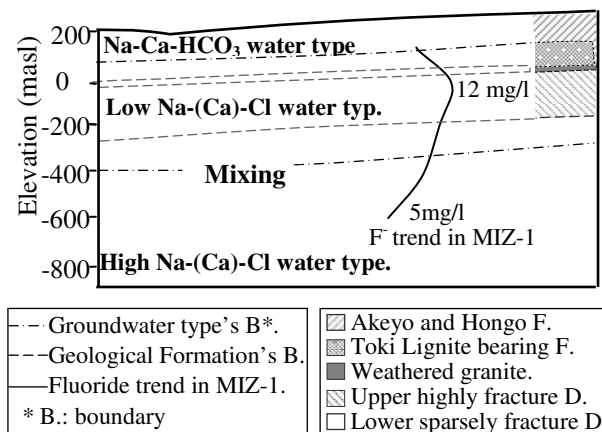


Fig. 2 Conceptual hydrogeochemical model in and around the MIU construction site. Rewrite after Iwatsuki et al.²⁾

evidenced in **Fig. 2**.

In the MIU construction site, excavation process of the shafts stopped at depth about 200 m due to the higher fluoride ion concentration than that of the Japanese environmental standard in the groundwater. From the general trend of fluoride ion concentration in MIZ-1 borehole, it is clear that fluoride ion concentration is high in low Na-(Ca)-Cl water-type. The present study is focusing on the evaluation of the increase of fluoride ion concentration in the MIU site.

3. EXPERIMENTAL METHOD

Four granite rock samples were collected from different depths of core of the MIZ-1 borehole, G1, G2, G3 and G4 their locations are 110.3, 150.10, 335.4 and 801.3 mabh (meter around bore hole), respectively. The granite specimen was crushed and powdered in a ceramic shatter box. The wet sieving was used to divide powder into three size fractions of 300-150, 150-75 and < 75 μm . Crushed granites were rinsed repeatedly with purified water.

Water-rock interaction tests were carried out within tightly capped conical glass flask under the room condition (temperature 20°C) at constant shaking-rate ~180 rpm. The low Na-(Ca)-Cl water-type is thought to be originated from rain water. With considering this point, tests were conducted using purified water with an initial pH value near 6.2. All batches were designed to have a constant water-rock ratio (10/1) and same size fraction for each set. The shaking time for each experiment continued for 30 days. Fluoride ion concentration and pH of the water samples were measured using ion selective method and pH meter, respectively, at the fixed interval time. The water samples (50 ml) were collected from the solutions after 3, 8, 12, 20, 30 days for each experiment. After finishing the experiment, the solutions and the

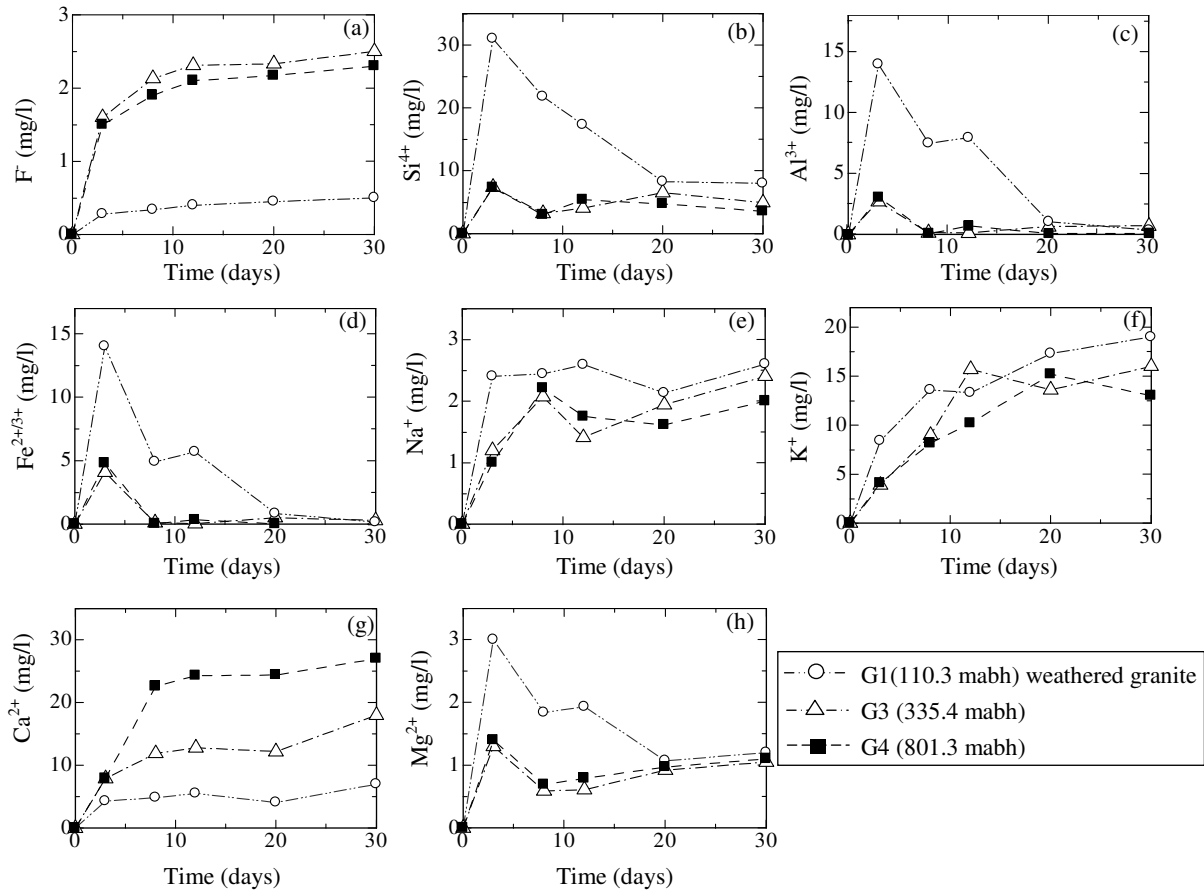


Fig. 3 Time series variations of the selected ions leached from granite. Size fraction 150-75 μm .

undertaken samples filtered with filter paper. The water samples were analyzed for chemical elements. The chemical analyses of cations concentrations were performed using Inductively-Coupled Plasma optical-emission spectrometry (VISTA-MPX). The anions concentrations were analyzed using ion chromatography (Dionex DX-120).

4. RESULTS AND DISCUSSION

(1) Water-rock interaction Test

The chemical analyses of the fluoride and some selected ions released from the three granite samples with time are illustrated in **Fig. 3**. At the beginning of the reaction time (3-5 days), the increase of the releasing concentrations of the most ions was relatively fast.

It was clearly observed that the F^- , K^+ , Na^{2+} and Ca^{2+} concentration ions are continuously increased with increasing the reaction time up to 10 days as shown in **Fig. 3. a, e, f and g**. This gradual increase indicated that K^+ , Na^{2+} , Ca^{2+} ions were continuously supplied by dissolution of feldspar. In general, there is good correlation between the release of the F^- and Ca^{2+} ions, indicating that the release of both ions is mainly due to dissolution of biotite and plagioclase, respectively. In turn, the weak correlation between

fluoride and potassium behavior revealed the influence of the source of potassium (i.e. K-feldspar or biotite) in the releasing process.

Chemical analyses of Si^{4+} , Al^{3+} , $\text{Fe}^{2+/3+}$ (total Fe) and Mg^{2+} ions has indicated that, at the first 3 days, the solubility of these elements in the weathered granite sample (G1) rapidly increased, and then it decreased with increasing the time as shown in **Fig. 3. b, c, d and h**. These results were inconsistent with other granite samples (G3 and G4). It is known that when granite is weathered, the plagioclase and K-feldspar undergo hydrolysis to form clay minerals (kaolinite or smectite). Cama et al.⁵⁾ concluded that the kaolinite dissolution rate is based on the release of Si^{4+} and Al^{3+} ions. These results were clearly evident with the weathered granite sample (G1). This finding might be verified the reason for changing the trend of fluoride ion concentration between first sample and other two samples because of occurrence of highly weathered in the top layer of granite.

In order to study the effect of change in the size fraction of granite powder on the leaching of fluoride ions from the granite samples, we carried out a series of experiments at the constant conditions such as room temperature, water-rock ratios and rock sample and different three size fractions of 300-150, 150-75 and < 75 μm .

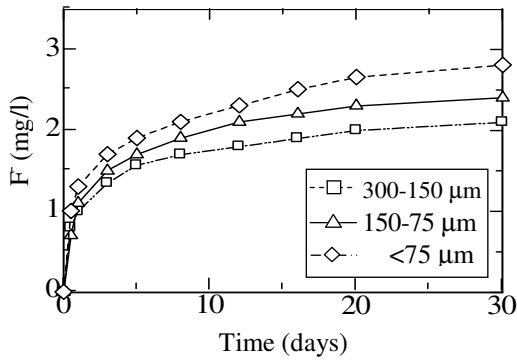


Fig. 4 Variation of leaching fluoride from granite per fraction size, sample G3 (335.4 mabh).

Fig. 4 shows results of three experiments with different size fractions from the same type of granitic rock. Results indicated that the finest size fraction showed the highest concentration of fluoride ions. This behavior might be due to the finest particle has the large surface area, so that might increase the effect of particle size. The small particle size of granite has the large surface area, so that the dissolution rate of fluoride ions in the water might be increased. However, the general results indicated that the effect of fraction sizes on the leaching of fluoride is not so large.

(2) Fluoride ion concentration in laboratory versus field condition

Our results show that the maximum value of the released concentration of fluoride ions from granite samples after 30 days shaking was about 3 mg/l. **Fig. 5** exhibits the comparison between the observed values from MIZ-1 borehole and the experimental data from the same borehole for both ions fluoride and chloride. The increased value in the fluoride ion concentration was shown in **Fig. 3. a**; however, the maximum value of fluoride ion concentration was observed in the field (12 mg/l) was shown in **Fig. 5. a**. Such results indicated that the interaction time among the water-rocks was substantially affected on the concentration of fluoride ion in the groundwater. **Fig. 5** reveals that the released amounts of the fluoride ions from the three granite samples, G2, G3 and G4, in different depths did not significantly change, despite the small amount released from the sample G1. The small amount of fluoride ion released from this rock sample might be due to the high weathering. This feature indicated that the fluoride amount is almost the same in most of unweathered granitic rock samples. In addition the concentrations of fluoride ions decreased with the depth in the field. One possible reason of this tendency is that the depth of the field might be mixed with two types of groundwater, such as low/high Na-(Ca)-Cl groundwater.

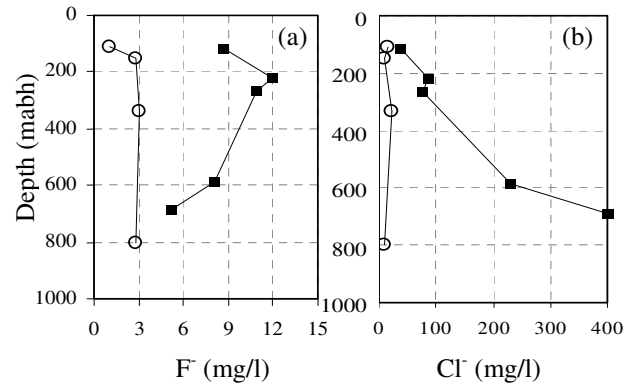


Fig. 5 Concentration of fluoride and chloride ions per depth in the MIZ-1 borehole.

- Results of the leaching experiments, 30 days shaking.
G1 (110.3 mabh) G2 (150.1 mabh)
G3 (335.4 mabh) G4 (801.3 mabh)
- Field data, Iwatsuki et al²⁾.

5. STATISTICAL AND STOCHASTIC ANALYSIS

A stochastic model was used in this study in order to evaluate approximately the complicated relation among fluoride ion concentration, co-existing of chemical components and reaction time. The variation in different granite specimens with the depths was neglected, as the first approximation.

The final goals for this statistical study are the approximation of the reaction time between granitic rock and groundwater. Moreover, the statistical study might estimate the parameters of the chemical components that affected released concentration of the fluoride ions.

In order to estimate the reaction time between groundwater and granitic rock, a time series data is needed. The results from the short-term of the interaction tests were combined with the field data. The field data used in this statistical analysis was collected from previous investigation in MIU site²⁾. As previously mentioned, the experiments were conducted using purified water. Therefore, the estimation of the reaction time has processed for the field data with only a low Na-(Ca)-Cl water-type.

First, from the short-term of the water-rock interaction tests, the approximated relation between fluoride ion concentration per mg/l and reaction time per days was adapted as a power functions. The best fitting parameters of the power function were estimated using least square method as shown in Eq.(1)

$$F^- = 1.24 * T_C^{0.18} \quad (1)$$

where, F^- is the fluoride ion concentration and T_C is the reaction time.

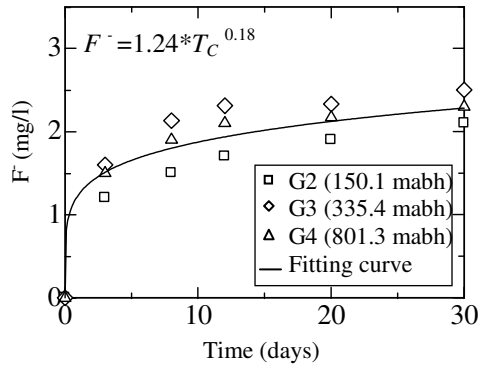


Fig. 6 The function between fluoride and reaction time.

Fig. 6 shows results of three experiments by using three granite specimens that collected from the different depths in MIZ-1 borehole and the fitting curve of these results. As previously mentioned that, the shallow granite is significantly weathered; therefore, our results did not show any statistical analyses from the first sample G1. A little deviation in the results might be due to spatial changing of the mineral composition for rock samples.

At the beginning, to consider the effect of other ions on F^- concentration, we assumed a linear empirical function between fluoride ion concentration and the effectively chemical parameters. Chemical analyses after the water-rock interaction tests showed that actively disturbance elements on the fluoride ion concentration are Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Si^{4+} , Al^{3+} , Cl^- , SO_4^{2-} and $Fe^{2+/3+}$. The contributions of these chemical parameters on the released F^- concentration were combined with the reaction time, as Eq.(2)

$$F^- = \sum_{i=1}^n \alpha_i C_i + 1.24 * T_C^{0.18} \quad (2)$$

where, C_i is the concentration of i -th ion, α_i is the parameter for each chemical components and n is the number of chemical components considered. The parameters were basically estimated according to Eq.(2), in which the time series of the experimental data were used. These unknown parameters were estimated using a spreadsheet optimizer (solver). Jon M. Wraith and Dani Or⁽⁶⁾ have provided a brief discussion about least square optimization by using solver. They also illustrated some of applications of this approach. From field

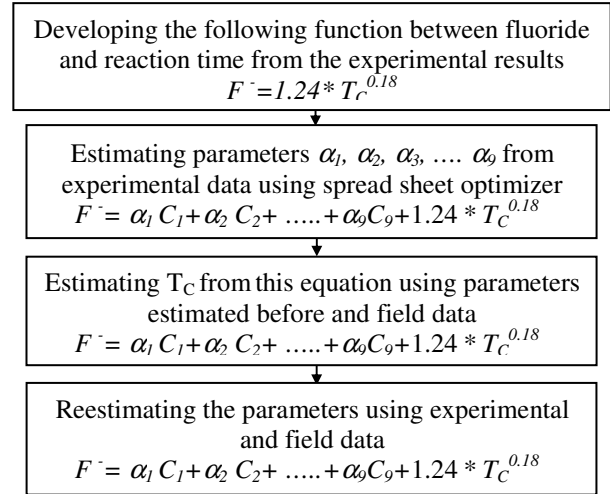


Fig. 7 Flow chart of the statistical analysis.

data, the reaction time was estimated on the basis of Eq.(2) by using the parameters that were estimated from experimental data. **Fig. 7** schematically shows the flow chart of the statistical analysis. The average value of the estimated T_C that showed a good fitting with the field data was approximated as 300 days for low Na-(Ca)-Cl groundwater type.

In order to verify this technique the sum square difference (SSD) was calculated between the calculated values of fluoride ion concentration (F_C^-) and the measured values of fluoride ion concentration (F_m^-), as Eq.(3)

$$SSD = \sum (F_C^- - F_m^-)^2 \quad (3)$$

the initial SSD value shows that there is small difference between F_C^- and F_m^- . This difference is owing to the short period of the reaction test. Due to this short period, the trend of some elements in respect to time can not simulate the real trend in the field data for the same element. In order to improve the convergence between calculated and measured fluoride ion concentration, the parameters have been re-estimated using the experimental data and field data.

Table 1 shows the values of estimated parameters before and after the correction. **Table 1** also shows the improvement in sum square difference (SSD) and coefficient of efficiency (CE) values after correcting the estimated parameters.

Table 1 Comparative performance of the convergence parameters.

Elements	Na^+	K^+	Ca^{2+}	Mg^{2+}	Si^{4+}	Al^{3+}	Cl^-	SO_4^{2-}	$Fe^{2+/3+}$	SSD	CE
Parameters estimated from experiments	0.144	-0.005	0.0198	-0.046	0.089	-0.151	-0.046	-0.095	-0.087	16.59	0.94
Parameters estimated from experiments and field data	0.092	0.0315	0.0012	-0.884	-0.041	0.041	0.052	-0.243	0.267	0.07	0.9998

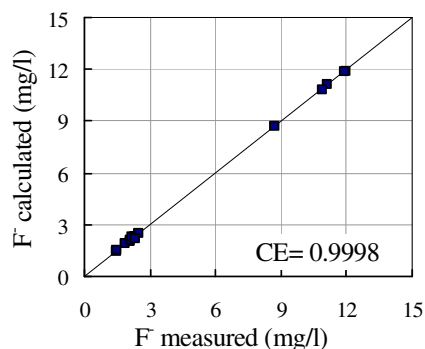


Fig. 8 Comparison between measured and calculated F^- conc.

Fig. 8 shows the comparison between the measured and the calculated fluoride ion concentrations. Within the correction, the coefficient of the efficiency (CE) value shows that the calculated fluoride ion concentrations was in good agreement with the measured fluoride ion concentrations, according to the experimental results and the field data for low Na-(Ca)-Cl water-type.

Fig. 9 shows the contributed effect of the co-existence of the chemical parameters and the reaction time on F^- concentration in five field data. These values were statistically estimated from experimental data and converged according to experimental data and field data from two boreholes MIZ-1 and MSB-4 at different depths for the low Na-(Ca)-Cl water-type. It is clear that the total contribution effect from the co-existence of the chemical parameters were about 70 % on fluoride ion concentration. The other 30 % is from the reaction time effect. Results indicated that, we can not neglect the effect of the co-existence of the chemical components on the leaching of fluoride ion from the granite.

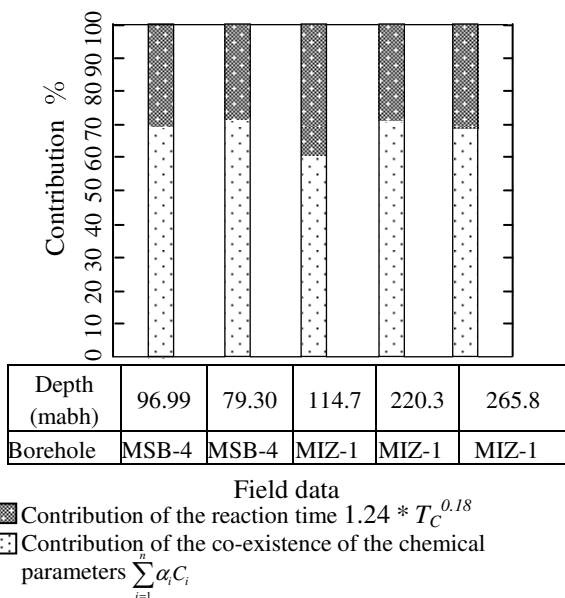


Fig. 9 Contributions of the co-existence of the chemical parameters and the reaction time on F^- concentration.

6. CONCLUSION AND FURTHER STUDY

The findings showed that the granite could act as a source of high fluoride ion concentrations due to the increase of the reaction time between groundwater and granitic rock. The fluoride ion released from highly weathered granite is relatively small. Our study shows promise to deduce the most active components affected on the fluoride ion concentration.

Statistical analysis for the data from short-term water-rock interaction test reported evidence of the evaluation of approximated reaction time that can be well fitting the field data as 300 days for the low Na-(Ca)-Cl water-type in the area around MIU site. The effect of the co-existence of the chemical parameters in fluoride ion concentration shows evidence of the significant contribution in the dissolution activity of fluoride ion in the groundwater.

Due to this technique had some approximations and assumptions; more experiments are needed to evaluate the chemistry of the groundwater by considering the mixing ratios between low/high Na-(Ca)-Cl water-types and by using the groundwater samples from the specific depths in different borehole.

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