



Inferring the chemical parameters for the dissolution of fluoride in groundwater of Bastar zone, Chhattisgarh, India

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Abstract

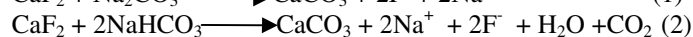
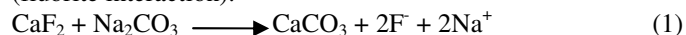
Physico-chemical data highlight that high content of F⁻ in groundwater of study area due to dissociation, decomposition and dissolution of fluoride-bearing minerals. Few physico-chemicals parameters also give positive correlation with F⁻ ion dissolution. These groundwater are alkaline in pH (7.54-8.55), HCO₃⁻ concentration varies from 266-370 mg/l and F⁻ concentration from 1.6-7.68 mg/l. Presence of F⁻ bearing mineral in bedrock is not only factor but physico-chemical environment like aqueous ionic species, residence time of interaction, chemical behavior of free F⁻ ion with other cations and anions in groundwater, play key role of its dissolution. This study indicates that 82% groundwater samples have EC- 940-1750 μS/cm and pH >7.8 Ionic concentration Ca²⁺, HCO₃⁻, Cl⁻ and Na⁺ in groundwater show strong positive relation with F⁻ ion concentration.

Keywords: Correlation, Dissolution, Hydrochemistry, Fluoride ion, Weathering.

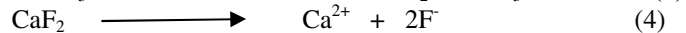
Introduction

The element fluorine has considerable physiological significance for human beings. Groundwater considered being major source of fluorine as fluoride ion (F⁻). Now a day's concentration of F⁻ ion in drinking water is burning issue. As per the WHO the permissible limit for daily intake of F⁻ ion in drinking water must be < 1.5 mg/l but above it may cause incurable disease fluorosis^{1,2}. From recent survey it has been found that nearly 600 million people around the world affected due to high F⁻ concentration in drinking water i.e > 1.5 mg/l³. According to Saxena and Ahmed et al maximum possibility of high F⁻ ion content in groundwater is natural process of weathering and dissolution of fluoride-bearing minerals in rock zone but exact mechanism still not well understood^{4,5}. Recent literature survey also indicate that anthropogenic activities like uses of excess of fertilizer, improper disposal of industrial waste also promote it⁶. It has been found that fluoride-bearing minerals are partially dissolved in water^{7,8}. Fluorine is highly electronegative element due to which free F⁻ ion is highly unstable and immediately form fluoride compounds and thus not causes any toxic effect. The aquifer condition and physico-chemical behavior of groundwater may provide favorable condition of its dissolution^{9,10}. There are so many fluoride bearing minerals found in rocks and earth crust. Among which fluorite (CaF₂), is most abundant and occurs in almost all rocks and accumulate in different minerals. From the study of atomic structure and chemical behavior of F⁻ and OH⁻ ions, both are almost similar ionic sizes and charges. It might be a one of the factor for the exchange of F⁻ ion with OH⁻ in groundwater. Apart from that, weathering, hydrolysis, dissociation, dissolution of minerals occur with time also promote it. The

possible mechanism of F⁻ in groundwater given by Saxena and Ahmed et al^{4,5}. According to that, if HCO₃⁻ ion is present as major content in the groundwater then the following type of reaction takes place during the water-mineral interaction (fluorite interaction).



From the above chemical reactions (1) and (2), it is clear that the NaHCO₃⁻ rich water in a weathered rock formation speed up the dissolution of CaF₂ to release F⁻ ion into the groundwater with time. pH play an important role for in these reaction and helps in dissolution of ionic species in groundwater. Aquifer which contain calcite (CaCO₃) as major minerals also promote the dissociation of F⁻ ion from F⁻ ion rich minerals, and this can be shown below in reaction (3) and (4):



$$K_{\text{eq}} = \{ (a_{\text{t}} \text{HCO}_3^-) \} / \{ a_{\text{t}}(\text{H}) * a_{\text{t}}(\text{F}) \} \quad (5)$$

Where: K_{eq} is an equilibrium constant, (Equation-5) and a_t is the activity of F⁻ ion which is directly proportional to HCO₃⁻ ion. Due to low solubility product of CaF₂, this relationship is independent.

In India, the literature survey highlights that high F⁻ in groundwater found to be geogenic rather than anthropogenic activities¹¹. The interaction of rock with water is the key chemical process in which fluoride-bearing minerals are decomposed and dissociated from the source rock and then free F⁻ ion is dissolved in the groundwater by dissolution^{4,8,12}.

The present work is an attempt to study the geochemistry of F⁻ ion in groundwater as well as to find the main physico-chemical parameters that enhance the dissolution activity of F⁻ ion in groundwater.

Materials and methods

The groundwater samples of 40 sampling point in Bastar zone with high F⁻ ion content were statistically analyzed. To find the possible factors of high content of F⁻ ion. An attempt to be taken, to observe the geochemical or hydro chemical mechanism for dissolution of F⁻ bearing minerals in aquifer of the study area.

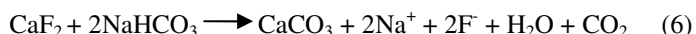
Results and discussion

Occurrences of F⁻ ion in Bastar zone: F⁻ ion occurs in various rock types such as granite, gneisses, quartzites, pegmatites, fluorapatite, cryolite, fluorite, biotite etc¹³. About 40 samples of groundwater have been selected from known F⁻ ion rich areas of Bastar zone in Chhattisgarh. Figure-1 shows study area graph with sampling point with high F⁻ ion content and physico-chemical data of those groundwater samples are presented in Table-1.

Chemistry of F⁻ ion in groundwater: The areas where groundwater is enriched in F⁻ (1.6-7.82 mg/l) are underlain by unusual types of geological formation which is confirmed by analyzed data as mentioned in Table-1. Main rock formations of the water sampling locations are Gondwana and sandstones etc. The old base comprised of granites, gneisses, pink pegmatites etc. Similarly, southern Gondwana consists of sandstone and most of the sampling locations are from the aquifers in confined/ semi-confined conditions in general in weathered and fractured zones¹⁴. It seems more appropriate that rock in F⁻ ion. From above data analysis it is very clear that more appropriate those rocks rich in F⁻ ion minerals have contributed to the enriched F⁻ ion concentration in groundwater during the course of weathering of rock types. It also appears more reasonable that dissolution activity of F⁻ ion minerals is more important for F⁻ ion concentration in groundwater rather than F⁻ bearing minerals

present in rocks. The decomposition, dissociation and dissolution process of fluoride-bearing minerals in rock types are responsible for high F⁻ content in groundwater. Including that, chemical environment and residence time also catalyzed the chemical reaction.

The dissolution activity rate of free F⁻ ion in groundwater differs for different rock types. Most of the fluoride-bearing minerals are moderately soluble in water under normal physical conditions of pressure and temperature. However, under certain physico-chemical conditions, activity of dissolution may become faster^{4,15}. From Table-1 it is clear that all the samples with high F⁻ ion content having pH values varied from 7.54-8.55 which indicate that all samples are alkaline in nature. The concentrations of different cations and anions in groundwater also influenced the free F⁻ ion solubility behavior. For example, in the presence of excessive NaHCO₃ in groundwater, the activity of dissociation of F⁻ ion will be abnormally high and possible chemical mechanism⁹ shown below as given Equation-6:



Analysis of the EC values of groundwater samples, it is observed that 90% of the samples are within the range of 940-1750 μS/cm (Table-1). Under normal pressure and temperature F⁻ ion can be easily replaced most of the anions^{16,17}. F⁻ ion has very less solubility products with Ca²⁺ ion, making the activity of dissolution more effective. Plots have been drawn between F⁻ ion content vs. Ca²⁺ ion concentration (Figure-2) and F⁻ ion vs. HCO₃⁻ ion concentration (Figure-3). Both plots show that there is a positive correlation with F⁻ ion. Thus, ionic species of this range may also provide a favorable chemical environment for the F⁻ ion dissolution process. From Table-2, it is clear that concentration of Na⁺ ion in groundwater strongly positively correlates with F⁻ ion concentration (R² = 0.75). It is also clear^{8,19} from chemical reaction 6. Physico-chemical parameters also influence the dissolution of fluoride-bearing minerals in groundwater^{6,15}. Concentration of Cl⁻, HCO₃⁻, EC, TDS show good positive relation with F⁻ ion.



Figure-1: Showing the Bastar zone of Chhattisgarh, India (Study area) Dots represent sampling point.

Table-1: The physico-chemical parameters results of groundwater sample with high F⁻ ion concentration in Bastar zone (study area).

GW	Village	Depth	pH	EC	TDS	Mg	Ca	Na	K	Cl	HCO ₃	SO ₄	F
Sample	Name	m(lpm)		μS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
GW1	Matwada	114	7.70	1163	646	37	35	125.4	38.8	102.5	140	130	3.12
GW2	Jangla	90	7.84	997	604	38	55	125.7	5.8	104.8	225	135	2.85
GW3	Kuchnur	154	7.87	1128	644	33	49	146.4	0.2	90	114	166	5.42
GW4	Adepalli	98	8.20	1276	729	45	72	112	0.8	84	235	172	2.12
GW5	Arkapalli	140	8.04	647	370	10	76	88.9	1.1	144	185	21	2.01
GW6	Muchler	105	7.66	922	527	34	78	81.2	2.3	115.5	202	102	1.55
GW7	Peta	144	7.75	903	516	32	46	91.4	2.8	114.4	102	82.3	1.74
GW8	Gulapenta	102	7.84	901	515	13	45	124	5.9	102	180	112	1.67
GW9	Chandagiri	96	7.92	927	530	48	32	104.1	6.4	102.5	109	50	1.88
GW10	Jabeli	86	7.66	909	519	29	35	80.9	33.5	42.3	156	148	1.58
GW11	Mendoli	90	8.12	1358	776	45	34	133.6	29.9	130	155	142	1.74
GW12	Mailawada	110	8.02	826	472	12	40	100.6	8.4	89.5	235	102	1.55
GW13	Masenar	89	7.88	722	412	4	20	105.6	10.5	115.9	115	23	1.68
GW14	Jaram	96	8.11	883	504	22	26	92	42.6	115	142	39	1.59
GW15	Gatam	104	7.84	1529	873	48	22	145	62.3	160	148	164	2.04
GW16	Chikpal	112	7.99	744	425	4	64	114.4	3.4	32.2	250	102	1.84
GW17	Renganar	90	8.01	898	513	28	20	134.9	32.6	96.3	190	48	2.32
GW18	Darapal	123	7.45	1218	696	33	39	166.9	1.8	155.3	202	105	2.01
GW19	Tarlapad	124	7.69	919	525	28	54	118.5	21.9	93.4	170	112	1.73
GW20	Pltepal	98	7.48	1464	592	28	30	115.2	0.3	155.4	124	66.6	2.05
GW21	Midkulnar	95	7.67	1066	537	25	52	90.2	1.2	126.5	205	60.5	2.1
GW22	Bakel	102	7.91	1365	780	15	50	204.3	1.2	188	222	152	4.58
GW23	Chhotejirak hal	116	7.68	1218	696	29	78	160.5	23.4	177	132	102	2.55
GW24	Karpawand	112	7.85	1090	623	25	39	141.2	0.3	180	142	75	3.47
GW25	Nandpura	181	7.84	1421	812	33	52	205.6	17.2	250	266	50	5.85
GW26	Turpura	125	7.91	1205	688	18	64	165.5	25.2	190	296	105	4.58

GW	Village	Depth	pH	EC	TDS	Mg	Ca	Na	K	Cl	HCO ₃	SO ₄	F
Sample	Name	m(lpm)		μS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
GW27	Dimrapal	167	8.02	1350	771	22	56	160.9	2.5	165.4	288	130.5	2.85
GW28	Bhosarrias	97	8.23	1017	581	14	46	106.9	12.5	142.2	274	92	1.93
GW29	Matnar	86	7.24	1042	632	14	32	146.1	3.2	92.5	190	106	2.88
GW30	Dilimili	95	6.96	847	514	29	46	90.1	12.5	100.5	256	102	1.68
GW31	Tekameta	108	8.33	1127	683	20	50	128.4	42.6	189	140	116	2.13
GW32	Vishrampur i	98	7.84	1168	675	28	62	134.1	47.5	222	200	76	3.85
GW33	Kesharpal	124	8.45	1284	745	40	68	162.8	0.3	202	266	86	4.14
GW34	Cherakpur	83	7.54	774	436	13	75	65.2	38.4	50.8	286	109	1.63
GW35	Borliyapal	115	7.09	716	434	28	22	70.5	3.4	60.2	115	95	1.89
GW36	Niyanar	102	7.11	991	547	44	46	84.8	1.9	90.2	125	95	1.88
GW37	Bagrai	108	7.15	745	451	25	32	82.4	20.8	89.3	148	42	2.24
GW38	Jaibel	156	8.24	1527	897	47	55	179.2	44.8	268.4	185	86.5	2.84
GW39	Garenga	106	8.08	1295	756	26	61	184.2	4.8	190.5	280	102.4	6.47
GW40	Barejirakhal	99	7.25	947	574	23	84	112.8	13.9	89.1	302	132	2.44

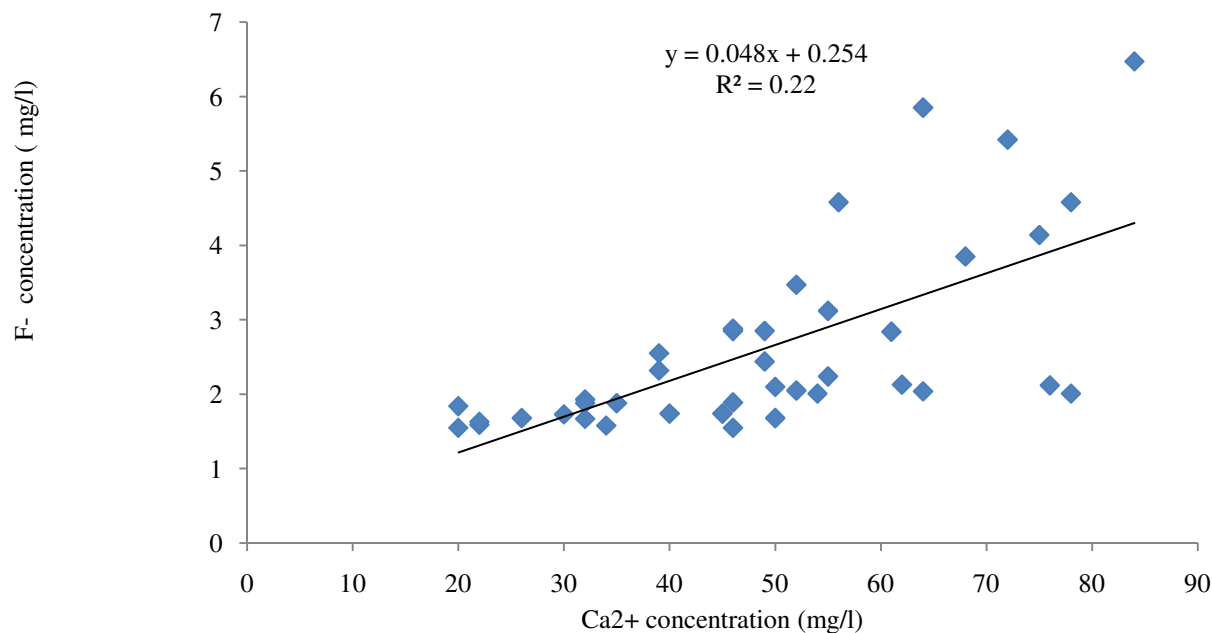


Figure-2: Plot showing F⁻ ion concentration vs. Ca²⁺ ion concentration correlation.

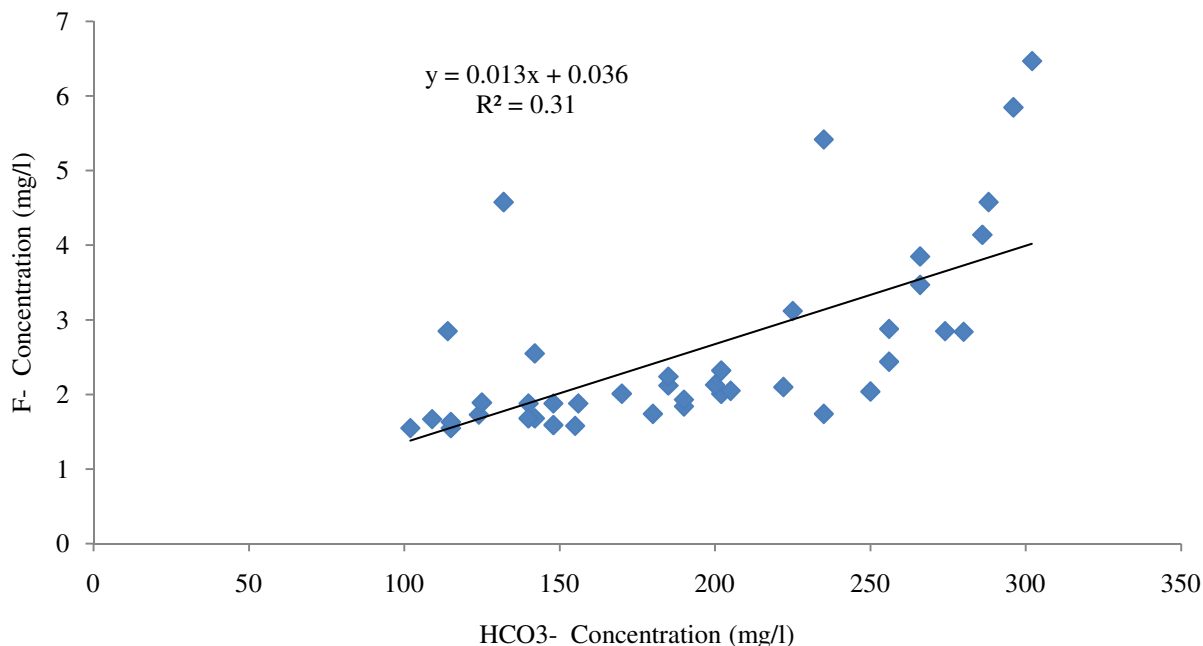


Figure-3: Plot showing the F⁻ ion concentration vs. HCO₃⁻ ion concentration correlation.

Table-2: The correlation matrix of different physico-chemical parameters of analyzed data.

pH	EC	TDS	Mg ²⁺	Ca ²⁺	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	F ⁻
	0.33	0.37	0.01	0.15	0.39	0.16	0.43	0.16	0.02	0.23
0.33		0.95	0.51	0.05	0.76	0.19	0.71	0.12	0.38	0.50
0.37	0.95		0.52	0.10	0.82	0.26	0.72	0.20	0.45	0.55
0.01	0.51	0.52		-0.08	0.14	0.19	0.20	-0.26	0.27	0.08
0.15	0.05	0.10	-0.08		0.11	-0.17	0.17	0.57	0.20	0.22
0.39	0.76	0.82	0.14	0.11		0.03	0.74	0.28	0.21	0.75
0.16	0.19	0.26	0.19	-0.17	0.03		0.19	-0.10	0.08	-0.10
0.43	0.71	0.72	0.20	0.17	0.74	0.19		0.16	-0.17	0.56
0.16	0.12	0.20	-0.26	0.57	0.28	-0.10	0.16		0.18	0.31
0.02	0.38	0.45	0.27	0.20	0.21	0.08	-0.17	0.18		0.11
0.23	0.50	0.55	0.08	0.22	0.75	-0.10	0.56	0.31	0.11	

Conclusion

Based on the calculation and observation of F⁻ ion variation and their analysis, conclusion comes out, high F⁻ ion in groundwater of Bastar zone is due to geogenic factors. Fluoride-bearing minerals like Fluorite (CaF₂), granitic and gneisses rocks and other minerals involve in rock-water interaction and liberate F⁻

ion into the groundwater. Physico-chemical parameters ranges as well as ratios are important during the dissolution process (pH: 7.54-8.55, EC- 940-1750 μS/cm. Cations and anions such as Na⁺, Cl⁻, Ca²⁺ and HCO₃⁻ are comparatively in good positive relation with F⁻ ions.

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