Annals of Arid Zone 25(4) : 255-264, 1986

OCCURRENCE AND CHEMISTRY OF HIGH FLUORIDE GROUND-WATERS IN JALORE DISTRICT OF WESTERN RAJASTHAN

S. C. GUPTA, C. S. DOSHI AND B. L. PALIWAL

Ground Water Department, Jodhpur - 342 003

ABSTRACT

Fluoride has been a veritable problem associated with ground-waters in western and south-west Rajasthan. More than 40 per cent ground-waters in Pali and Jalore district contain fluoride concentration above the permissible limits of 2.0 mg/l. The ground-waters in the region are saturated with respect to calcite and about 27 per cent of them have fluoride concentration above the solubility product for fluoride. High fluoride waters have, in general, high sodium and bicarbonate contents; however, such relationship does not hold true on the principles of chemical thermodynamics.

INTRODUCTION

Fluorosis has become a growing scourge in Rajasthan with nearly 350,000 people suffering from this crippling disease. The disease is caused by high fluoride contents of ground-waters which occur almost all over the state (Paliwal *et. al.*, 1969; Singh and Sinsinwar, 1975; Gupta, 1982 and Ram Gopal and Ghosh, 1985). In the districts like Pali and Jalore in the south-west, more than 40 per cent of ground-waters contain fluoride above the maximum permissible limits of 2. 0 mg/l for drinking waters. In this paper, an attempt has been made to characterise the chemical properties of high fluoride ground-waters occurring in Jalore district on the principles of chemical thermodynamics.

MATERIAL AND METHODS

Ground-water samples from nearly 165 dug wells representing different hydrogeological formations in Jalore district were collected during the years 1976-1982 and analysed chemically using APHA standard methods of chemical analysis (Anon., 1976). The fluoride estimations were carried out spectrophotometrically using Alizarin red and Zirconium oxychloride reagents. The average chemical composition of ground-waters in the district has been calculated and is shown in table 1. The activity of fluoride and other related ions was calculated by Debye-Huckle equation.

Table 1. Ionic composition of ground-waters in Jolore district (mean of 165 samples)

EC μS/cm	pH	Ions (me/l								F^-
		Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	mg/l
4928	7.8	35.9	1.4	6.4	7.8	34.7	6.6	8.5	1.7	2.35

Location, hydrogeology, physiography & drainage

Jalore district is characterised by extreme climate and low rainfall (av annua precipitation 379.86 mm). Luni river and its tributaries wnich cover the district are all ephemeral. Lithologically the district is composed mainly of younger and older alluvium of recent, sub-recent to pleistocene periods followed by post-Delhi intrusives of rhyolites and granites (both Erinpura and Jalore series). Clays and silts with intercalation of medium to coarse sand and gravel of tertiary period are also encountered in the exploratory drillings e.g. at Jodhawas and Batera etc. towards western parts of the district (Henry *et al.*, 1983). The ground-water generally occurs under water table or semi-confined conditions. The depth to water table varies considerably ranging from 0.8 to 45.0 m below ground level (bgl) but, in general, it occurs in 5 to 15 m bgl. The common rock minerals are feldspars, quartz, biotite, apatite and hornblende. The well known fluorite deposit also occurs near Karda in Bhinmal block. High fluroide ground-waters occur throughout the district but quite commonly in Ahore, Bhinmal, Jalore and Jaswantpura blocks where older alluvium is overlain to granite.

Chemistry of fluoride in ground-water

Fluoride is an inherent, 10th rank component of the igneous rocks and has an average value of 715 mg/kg (Hem, 1985). Fluorite (CaF_2), apatite [$Ca_{10}F_2$ $(PO_4)_6$] and cryolite (Na_8AlF_6) are the main fluoride bearing minerals in igneous, metamorphic and sedimentary rocks. In minerals like mica, amphiboles and topaz etc. the fluoride ions are bound on the mineral surfaces and can be displaced by hydroxyl ions with rise in pH.

In water, fluoride occurs mainly as F^- ions and may form strongly soluble complexes with aluminium, beryllium and ferric iron. In presence of boron, mixed fluoride-hydroxide complexes are formed. At pH below 3.5 the HF^0 form may occur. Handa (1975) made a thermodynamic approach to study the occurrence of fluoride ions in presence of calcite equilibrium and correlated high fluoride concentration with increase in bicarbonate ions in ground-waters of nearly constant pH. Considering the calcite and fluorite equilibrium reactions, we have:

$$CaCO_3 + H^+ = Ca^{2+} + HCO^-_3$$

$$\text{and } K_{\text{calcite}} = \frac{[Ca]\,[HCO_3]}{[H]} \qquad \ldots (1)$$

Similarly,—

$$CaF_2 = Ca^{2+} + 2F^-$$

$$\text{or } K\text{Fluorite} = [Ca^{2+}]\,[F^-]^2 \qquad \ldots (2)$$

By dividing equation (1) by (2) we get:

$$\frac{[HCO_3]}{[H]\,[F]^2} = K \text{ (constant)} \qquad \ldots (3)$$

$$\text{or} \qquad F^2 = K' \frac{[HCO_3]}{[H]} \quad \left(\text{where } K' = \frac{1}{K}\right) \ldots (4)$$

$$\text{and} \qquad F^- \propto \sqrt{\frac{[HCO_3]}{[H]}} \qquad \ldots (5)$$

From equations (2) and (3) it is apparent that the fluoride activity is largely controlled by calcium and bicarbonate content particularly in a constant pH range. The solubility of fluorite is very low ($K_{sp} = 10^{-10.57}$ at 50°C) and for an activity of 40 mg/l of Ca^{2+} ions the equilibrium activity of F^- would be 3.2 mg/l, but the concentration may be higher in presence of other dissolved constituents. Thus in ground water system where the number of variable constituents are comparatively more, the high fluoride concentration would be favoured by low calcium content and high bicarbonate value or, in other words, by a high bicarbonate to calcium ratio but low calcium to other cations ratio.

RESULTS AND DISCUSSION

1. *General chemical characteristics of ground-water*

The mean chemical composition of ground-water in Jalore district is shown in table 1. The fluoride concentration varied from nil to 14.2 mg/l. High concentrations of fluoride were observed all through the district, but in four blocks namely Ahore, Bhinmal, Jalore and Jaswantpura the intensity of distribution was relatively high. In certain villages, as Kawarda in Ahore and Medauparla in Jalore blocks, the fluorosis was perceptible in humans as well as livestock.

It was further observed that the high fluoride values were not confined to granitic formations only but were evenly distributed also in other formations they (Table 2).

Table 2. Fluoride distribution in different hydrogeological formations in Jalore district

S.No.	Hydrogeology	No. of Samples	Fluoride (mg/l)		
			min	max	av
1.	Younger alluvium	47	nil	14.2	2.47
2.	Older alluvium	95	nil	8.0	1.86
3.	Granite	20	0.64	5.0	2.67
4.	Rhyolite	3	1.00	3.6	2.09

Unusually high fluoride values in Quaternary formations can be accounted obviously because these formations overlied granites and Malani Volcanics in the region and thus had common mineral distribution.

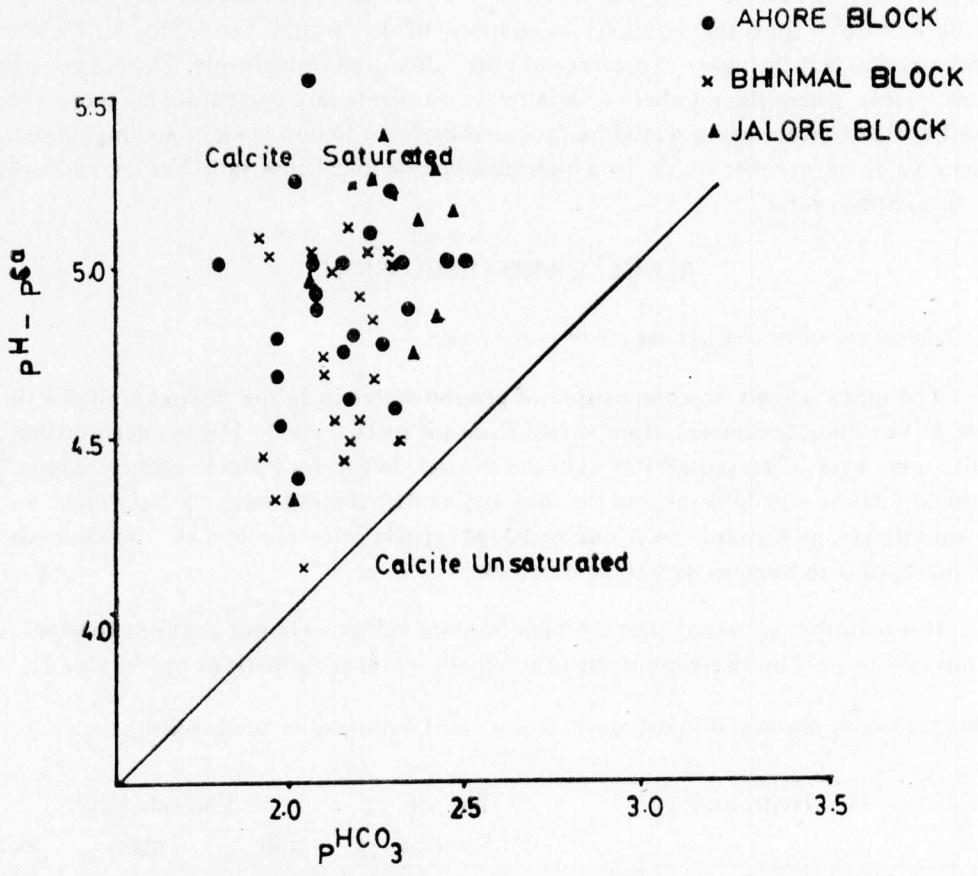

Fig. 1. Calcium and bicarbonate equilibrium in groundwaters of Jalore district.

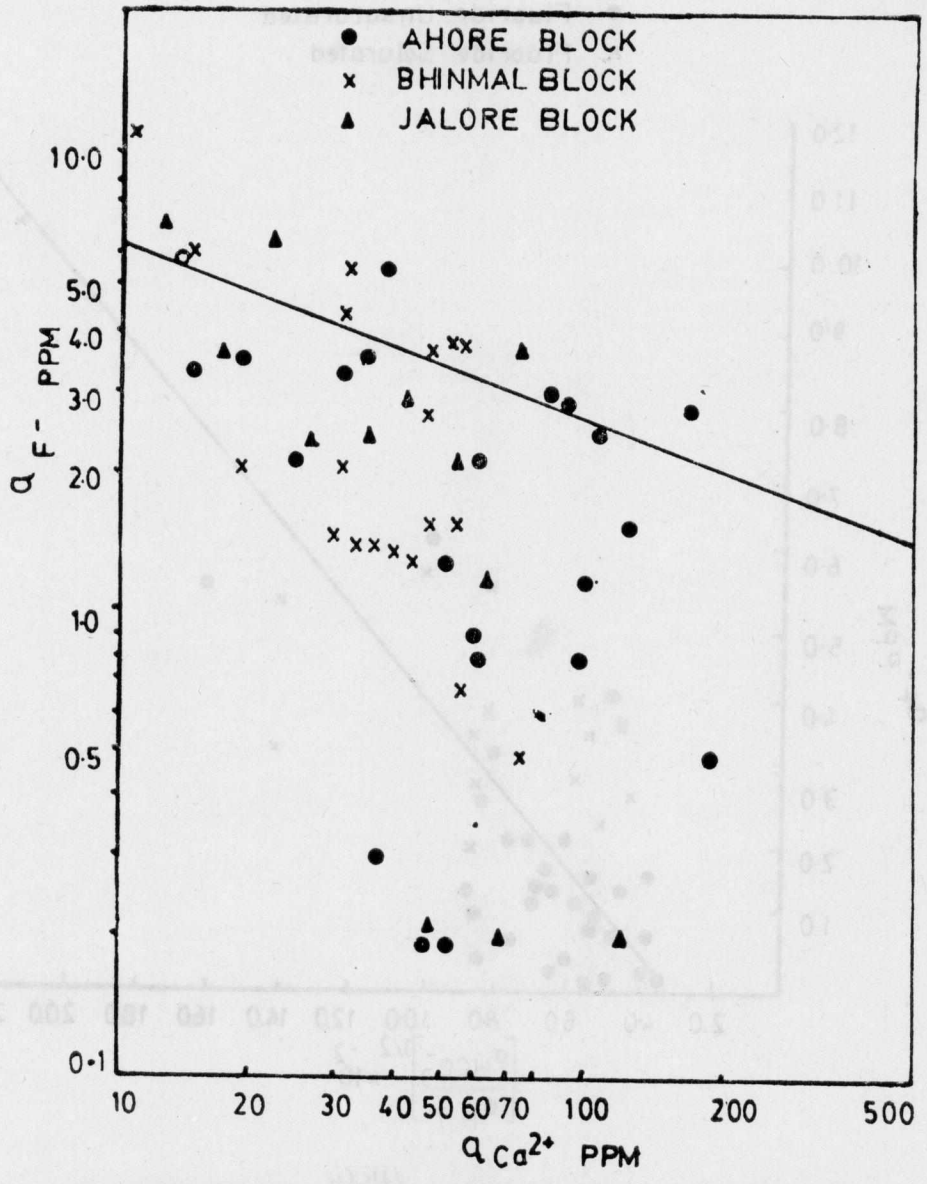

Fig. 2. Saturation of grouud-waters with respect to fluorite in Jalore district.

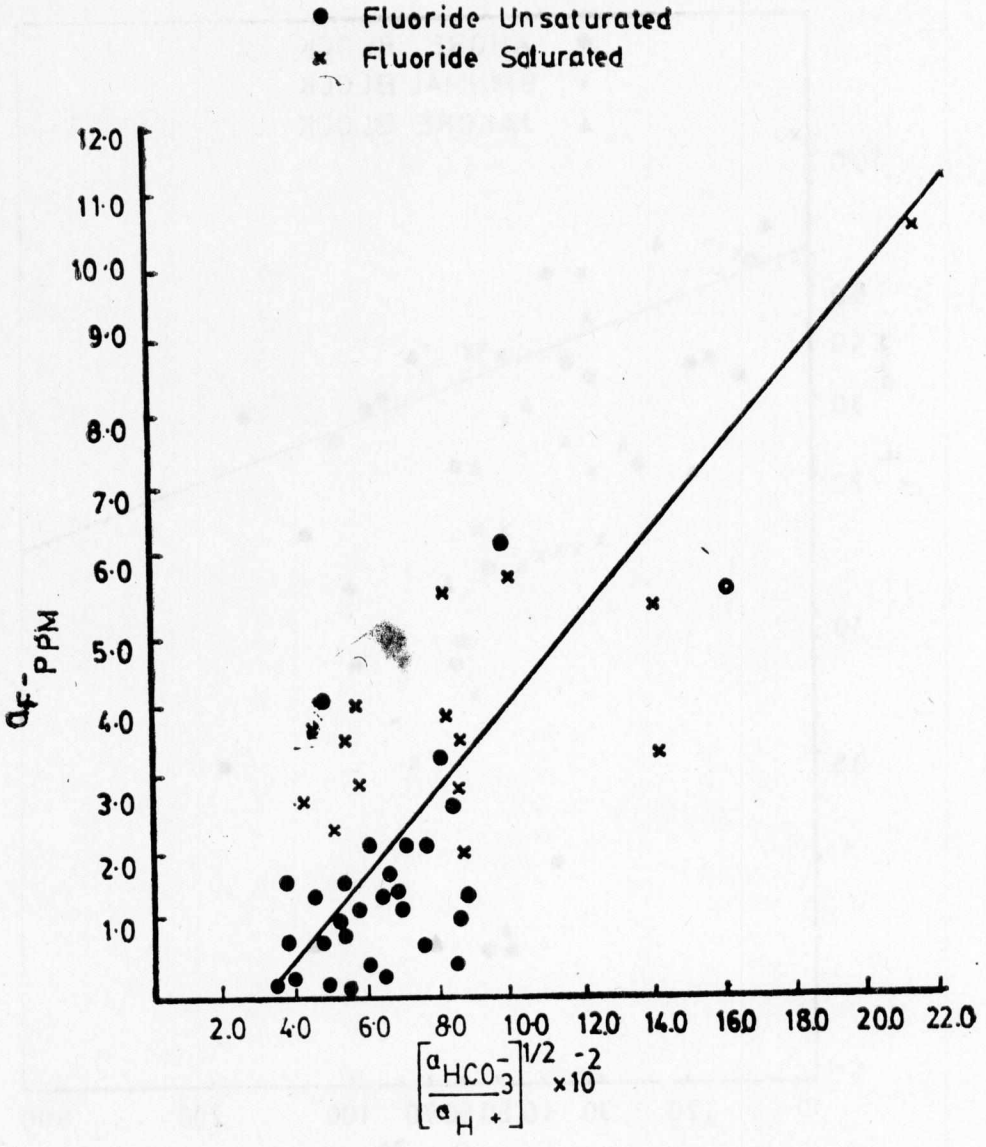

Fig. 3. Fluoride variability with respects to $\sqrt{\frac{HCO_3}{H}}$ in ground-waters of Jalore district.

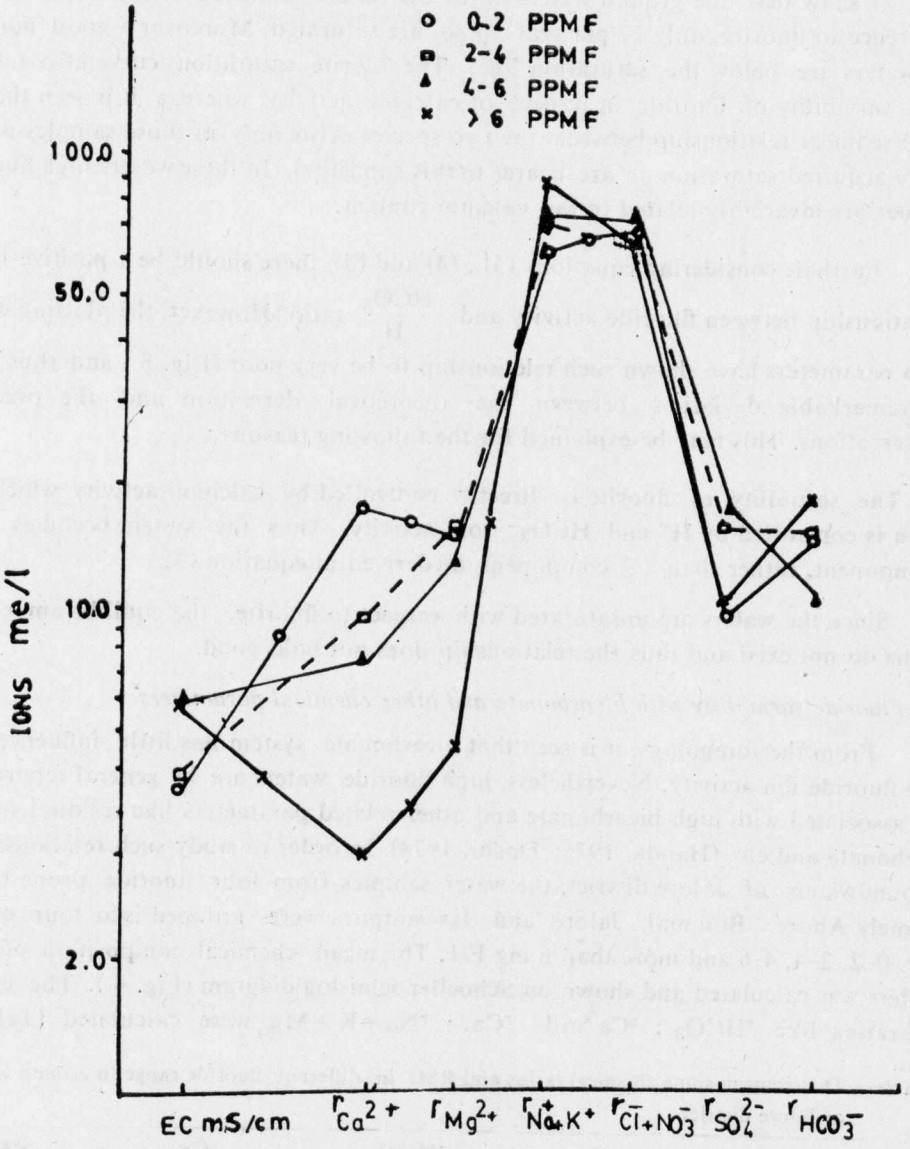

Fig. 4. Schoeller semi-log diagram showing mean chemical composition of ground-waters in different fluoride concentrations.

2. *Thermodynamic relationship and saturation index*:

The plottings of ionic activities in relation toc alcite and fluorite saturation (Figs. 1 & 2) show that the ground-waters in the distict are saturated with calcite but with reference to fluorite, only 27 per cent or so are saturated. Moreover a good number of waters are below the saturation line. The fluorite saturation curve also reflects the variability of fluoride in respect of calcium activity, whereas it is seen that an inverse linear relationship between the two species exists only in those samples which have acquired saturation or are nearer to this condition. In these waters high fluoride values are invariably related to low calcium content.

Further, considering equations (3) , (4) and (5), there should be a positive linear relationship between fluoride activity and $\frac{HCO_3}{H}$ ratio. However, the plotting of the two parameters have shown such reletionship to be very poor (Fig. 3) and thus there is remarkable deviation between the theoretical derivation and the practical observations. This may be explained for the following reasons :

i. The solubility of fluorite is directly controlled by calcium activity which, in turn is controlled by H^+ and HCO_3^- ion activity. Thus the system becomes a 4–component, rather than a 3–component, as derived in equation (3).

ii. Since the waters are unsaturated with respect to fluorite, the equilibrium conditions do not exist and thus the relationship does not hold good.

3. *Fluoride variability with bicarbonate and other chemical parameters*

From the foregoings, it is seen that bicarbonate system has little influence over the fluoride ion activity. Nevertheless, high fluoride waters are in general reported to be associated with high bicarbonate and other related parameters like residual sodium carbonate and etc. (Handa, 1975; Doshi, 1974). In order to study such relationship in groundwaters of Jalore district, the water samples from four fluoride prone blocks namely Ahore, Bhinmal, Jalore and Jaswantpura were grouped into four classes viz. 0–2, 2–4, 4-6 and more than 6 mg F/1. The mean chemical composition of these waters was calculated and shown on Schoeller semi-log diagram (Fig. 4). The chemical ratios like $^rHCO_3 : {}^rCa$ and $^rCa : {}^rNa+K+Mg$ were calculated (Table 3)

Table 3. Distribution some chemical ratios and RSC in different fluoride range in ground waters of Jalore district

F^- range (mg/1)	No. of Samples	$\frac{^rHCO_3}{^rCa}$	$\frac{^rCa}{^rNa_+ K_+ Mg}$	RSC (me/1)
0.2	35	1.61	0.26	0.66
2-4	22	2.71	0.18	1.48
4-6	13	2.55	0.13	1.87
>6	7	8.42	0.04	7.91

along with RSC values in each fluoride class. The fluoride variation with respect to bicarbonate ions was also plotted (Fig. 5). From these figures and table 3 the following important observations are made:

i. Significant decrease in calcium concentration in relation to increase in fluoride content is in line with the theoretical assumptions.

ii. In high fluoride range a sudden drop in magnesium percentage is seen (Fig 4). The solubility of MgF_2 is much higher than CaF_2 (K_{sp} $=7.0 \times 10^{-9}$) but its precipitation in high fluoride waters cannot be ruled out.

iii. A regular increase in sodium precentage is seen with increase in fluoride values. In fact most of the waters with fluoride content above 5.0 or so are having sodium percentage above 80. The high fluoride content in association with high sodium percentage were also observed by Sanganeria *et al.* (1983) in ground-waters of Pali district and Raju *et al.* (1983) in ground-waters of Penner Basin in Andhra Pradesh The high fluoride values in relation to high sodium percentage can be accounted for high degree of mineral weathering.

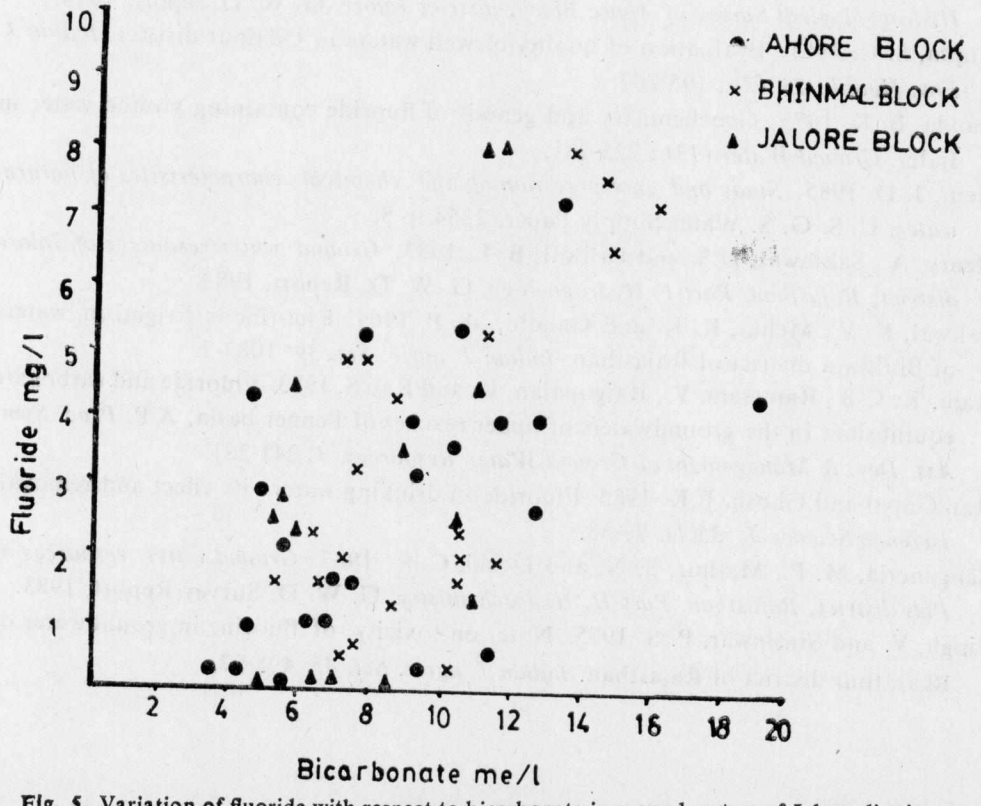

Fig. 5. Variation of fluoride with respect to bicarbonate in ground-waters of Jalore district.

iv. The plotting of F^- vs HCO_3^- (Fig. 5), though shows a general positive correlation, is simultaneously characterized by high degree of scattering. The same could, therefore, be accounted more on the theoretical grounds rather than on thermodynamic principles as inferred by Handa (1975). The high bicarbonate waters, in general, have relatively high pH and have a tendency to displace F^- ions from the mineral surface as described earlier. A sudden change in chemical ratios is thus seen only in high fluoride waters (Table 3). The highest value of fluoride (14.2 mg/l) was also observed in the well water having highest pH (8.6) and very high bicarbonate content (15. 0 me/l)

ACKNOWLEDGEMENTS

The authors are grateful to the Chief Engineer, Ground Water Department, Jodhpur for according necessary permission for publication of the paper.

REFERENCES

Anonymous, 1976. *Standard methods for the examination of water and wastewater.* American Public Health Association, Washington, D. C. 20036.

Doshi, C. S. 1974. Chemical quality of ground water. *Report on the Reconnaissance Hydrogeological Survey of Ahore Block, district Jalore.* G. W. D. report, 1974,

Gupta, S. C. 1981. Evaluation of quality of well waters in Udaipur district. *Indian J. Env. Health. 23 (3)* : 195-202.

Handa, B. K. 1975 Geochemistry and genesis of fluoride containing ground water in India. *Ground Water (13)* : 225-281.

Hem, J. D. 1985. *Study and interpretation of the chemical characteristics of natural water.* U. S. G. S. Water Supply Paper, 2254. p 5.

Henry, A., Saktawat, U.S. and Paliwal, B. L. 1983. *Ground water resources of Jalore district, Rajasthan. Part-I, Hydrogeology.* G. W. D. Report, 1983.

Paliwal, K. V , Mehta, K. K. and Gandhi, A. P. 1969. Fluorine in irrigation waters of Bhilwara district of Rajasthan. *Indian J. agric. Sci. 39*: 1083-7.

Raju, K. C.B., Ramesam, V., Rajgopalan, K. and Rao S. 1983. Fluoride and carbonate equilibrium in the groundwaters of upper reaches of Penner basin, A.P. *Proc. Sem. Ass. Dev. & Management of Ground Water Resources. 3:* 241-281.

RamGopal and Ghosh, P.K. 1985. Fluoride in drinking water –its effect and removal. *Defence Science J. 35(1)*: 77-88.

Sanganeria, M. P., Mathur, S. N. and Doshi, C. S. 1983. *Ground water resources of Pali district, Rajasthan. Part-II, Hydrochemistry.* G. W. D. Survey Report, 1983.

Singh, V. and Sinsinwar, P. S. 1975. Note on toxicity of fluorine in groundwater of Bharatpur district of Rajasthan. *Indian J. agric. Sci. 45:* 495-97.