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Geochemistry of Fluoride Enrichment in groundwater: A critical review of the Indian regime

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Abstract
Groundwater is one of the natural resources having its application in various fields, which affects its quality. Fluoride-enriched water has become a major public health issue in various parts of the world. The geochemical mechanism of the fluoride enrichment in drinking water needs to be evaluated. Groundwater quality is controlled by rock-water iteraction, residence time of water in aquifers, and anthropogenic factors at many locations. Dissolution of fluorite and fluorapetite minerals in earth & simultaneous precipitation of $CaCO_3$ *is considered to be among the mechanisms responsible for it. The simultaneous increase in alkalinity of the water with high fluoride levels must be co-related. Due to Ca2+ and Mg2+in, the hardness of the water is responsible for precipitating fluoride from groundwater. Major geological formations where an excessive concentration of fluoride has been reported are sedimentary rocks and metamorphic granites such as shale, limestone, granite, charnokite, BGC gneiss. Climatic conditions, hydro-geological surroundings, physical factors (temperature and rainfall), geochemical processes such as weathering, evaporation, dissolution, and ion exchange are the prominent causes for the elevated concentration of fluoride in aqueous solutions.*

Keywords: *Hydro-geochemistry, fluoride contamination, precambrian, rock-water interaction, fluorite.*

I. GROUNDWATER CHEMISTRY

To understand the hydro-geochemistry of an aquifer, deep insight into rock-water interaction that governs the groundwater chemical composition needs to be studied. The mineral composition of the rock is the prime factor that regulates the water chemistry of a location. Due to the continuous interfacial reaction of water with rocks, the local regime has a distinct composition from other locations.

Among various aspects like evaporation and concentration, dilution due to precipitation contributes to managing groundwater's chemical composition. The solid inorganic and organic matter present in the rocks upon interaction with water is responsible for the dissolution/deposition of groundwater constituents. When the groundwater moves along recharge to discharge areas, different chemical reactions with solid segments take place. The geological formations of an area and residence time of the groundwater interaction initiate the chemical reaction spatially and temporally. The time interval of rock-water interaction and associated chemical reactions constitutes the dissolved ions of groundwater. The major ions present in groundwater can be used to predict the duration of its interaction with parent rock. The genesis of fluoride, now considered one of the contaminants in different parts of the world, is often associated with the dissolution of fluorine-containing minerals in the rocks, besides emerging anthropogenic factors. Mineral water interfacial reactions like carbonate weathering and dissolution, silicate weathering, and ion exchange processes contribute towards groundwater chemistry [1]. Hydrogeochemical processes such as dissolution, cation exchange processes, calcite equilibrium, and residence time along with the flow path control groundwater composition in the shallow alluvial aquifers [2],[3]. Leaching of salts from surface, ion exchange processes, and residential time causes hydro-geochemical variations of groundwater from a semiarid sedimentary basin [4].

The concentration of ions in groundwater may change due to various chemical processes such as hydration and hydrolysis, weathering and deposition, ion exchange processes, oxidation, and reduction occurring during mineral-water interaction. These reactions impacted the mobility of the dissolved constituent & change the pH of groundwater at various locations. An elevated concentration of fluoride (4.24 ppm) was detected in Pokhran, Rajasthan. The highly alkaline groundwater conditions were interpreted as the major process responsible for fluorite dissolution [5].

II. ROCK WATER INTERACTION

The groundwater quality is managed by the mineral composition of the rocks [6]. Groundwater quality mapping and its evaluation have been reported worldwide using GIS [7]-[10]. Rock-water interaction was identified using total dissolved solids (TDS) vs. Na/(Na + Ca) and TDS vs. Cl/(CI + HCO_3) as reported by Gibbs [11]. Minerals present in different rock types like igneous, metamorphic, and sedimentary completely or partially dissolve in water according to the resistance or ease of chemical weathering. Quartz-cemented sandstone, silt, slate, shale, schist, gneiss, and quartzite have high to very high resistance towards chemical weathering. Simultaneously, calcite cemented sandstone, limestone, rock salt, Gypsum, Marble and basalt have low to moderate resistance to chemical weathering. As a result of these interactions, different minerals like halite, pyrite, gypsum, dolomite, and calcite show good water dissolution. Olivine, Pyroxene, hornblende, biotite due to moderate resistance dissolves in water by oxidation-reduction and hydrolysis processes. Feldspar, qartz, clay, due to high resistivity towards weathering, dissolves very slowly in groundwater. As a groundwater contaminant, among various other minerals, fluorite and fluorapetite are considered as the potential sources of fluoride [12]-[16].

Fluoride is only found as fluorite (CaF_2), usually an accessory mineral of granitic rocks (Kundu et al., 2001). Water discharging through granitic rocks has an average fluoride content of 810 mg/l, higher than water flowing through metamorphic and sedimentary rocks [17]-[19].

III. DISSOLUTION/PRECIPITATION OF MINERALS

In a dissolution and/or precipitation, the mass transfer occurs between rock types and groundwater [20]. Dissolution leads to starts when groundwater reaches equilibrium. A saturated solution is at equilibrium, at which the rate of dissolution and re-depositing are the same. Suppose the concentration becomes less than the saturation point during the weathering process. In that case, minerals dissolve from rock and form groundwater constituent & when in excess, mineral components may combine to form a precipitate. Coupling of dissolution/precipitation at the mineral fluid interface maintains this equilibrium condition [21]. Calcite ($CaCO_3$) precipitation and after that fluorite (CaF_2) and/or fluorapatite (FAP) [$Ca_5(PO_4)_3F$], dissolution may be the dominant mechanism responsible for groundwater fluoride contamination. Dissolution of fluorite (and FAP) increases by calcite precipitation in alkaline solution (Eq.1). This takes out Ca^{2+} from the solution, thus reducing the aqueous Ca^{2+} activity [22]-[25].To maintain the equilibrium conditions, fluorite mineral dissolves, thus increasing fluoride ion concentration in solution (Eq.2).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O \qquad (1)$$

$$CaF_2 \rightarrow Ca^{2+} + 2F^- \qquad (2)$$

Due to the common ion effect, the dissolution of fluorite is suppressed at locations where calcium hardness is reported to be above the limit for fluorite solubility [26]. There is a negative correlation between Ca^{2+} and F^- in groundwater that contain Ca concentrations in excess of that required for fluorite solubility [27]. Removal of Ca^{2+} can also be achieved by ion exchange (with Na^+) from clay minerals; thus, showing a strong positive correlation between Na^+ and F^- [28]. This changes the solution's saturation state, which increases fluorite/FAP dissolution & thus enhances the concentration of F^- in the water. A high concentration of fluoride, i.e., about 8 – 10 mg/l in groundwater due to fluorite dissolution, is possible in waters of low ionic strength[18]. The solubility of fluoride is also affected by the aqueous ionic concentrations of groundwater. In the presence of excessive sodium bicarbonates in groundwater, the dissociation of fluoride will be high due to the precipitation of $CaCO_3$, and this can be expressed as:

$$CaF_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2Na + 2F + H_2O + CO_2$$

Hydro-geological investigations of Alleppey in Kerela have revealed that the groundwater is $Ca\text{-}HCO_3$ type and changes to Na-HCO3 type in some areas. Initially, $Ca\text{-}HCO_3$ type water was formed by the chemical reaction of rainwater containing CO_2 on $CaCO_3$ bearing minerals in the recharge zone. During its movement, the water exchanges Ca for Na by the ion exchange process. This resulted in $Na\text{-}HCO_3$ type water, which also explains the higher fluoride content in the Alleppey area since the alkaline water depleted in Ca effectively releases fluoride from the minerals fluorapatite [29].

IV. GEOLOGICAL FORMATIONS

Among various minerals abundant in fluorides like apatite, mica, amphiboles, and clay, fluorite (CaF_2) is the major mineral occurring in nature and is commonly found in granitic gneiss [30]-[33]. The archaeans/palaeoproterozoic rocks are comprised of granite gneisses, metasedimentary rocks, quartzites, pegmatites, brecciated quartzites, etc. Lower gondwanas consist of sandstones and shales, whereas Deccan traps consist of basalts and dolerites. These rocks comprise mainly silicates of Na, K, Al, and Ca, which are the precursors of fluoride release in groundwater. Besides this, it appears that fluoride minerals' dissolution activity is more important for fluoride concentration in groundwater than fluoride-bearing minerals present in rocks.

The dissolution of fluoride minerals in groundwater from rocks differ from one another. Under normal temperature and pressure, fluorite and cryolite are sparingly soluble in water. Some Physico-chemical conditions, like dissolution, may activate the process to a faster mode [34]. Acidic pH helps fluoride get absorbed in clay; however, desorption occurs in an alkaline medium. Thus alkaline pH is favorable for fluoride dissolution activity.

V. FLUORIDE CONTAMINATION IN TERRAIN OF INDIA

Precambrian age granite rocks like quartzite, cherty dolomite, shale & limestone form the denudational hills in Andhrapradesh. Weathering of these rocks formed brown loamy soil of high alkalinity. A high concentration of fluoride has been reported in the groundwater present in fractured hard rock zone with pegmatite veins of this area [35]. Fluoride contaminated groundwater with a maxi. The concentration of 4.8 mg/l has been reported in the Yadgir district of Andhrapradesh, having peninsular gneiss and granite terrain [36].

The Fractured granite and granitic gneisses of late archean to early Proterozoic era are well known for high fluoride-rich minerals like fluorite, biotite, and hornblende content in them forms the basic terrain of Nalgonda in Telangana [37]-[40]. This is overlaid by quartzite, shale, and limestone of the cuddapah supergroup. The area's Pambar river basin is made of Archaen gneissic and charnockitic basement with igneous intrusions of Proterozoic age [41]. These rocks contain fluoride-rich minerals, and the weathering of these rocks leads to the release of fluoride into groundwater [42],[43]. The groundwater of Alleppey, Kerela, having a high concentration of fluoride, has sedimentary rock formation underlain by Precambrian crystalline basement and overlain by laterites and alluvium [44]. The hydrochemical profile shows a decline in calcium content with a simultaneous increase in sodium. Bicarbonate dominated the anionic constituent. The resulting Na-HCO_3 type of water explains the higher fluoride content in the area [29].

A study of geochemical enrichment from India's western part revealed the higher concentration of fluoride in groundwater due to Na-Cl-HCO3, Na-Ca-Cl-HCO3, Na-Cl Na-Ca-Mg-Cl-HCO_3 regime in water [45]. Na and HCO_3 are the major components in all the water types responsible for dissolving fluoride from fluorite. Thus fluoride concentration increases in water. Siddipet of Telangana state is occupied by granites of the Archean age. Hydrogeochemical investigation in groundwater samples of the area revealed F-in groundwater concentration, ranging from 0.2 to 2.2 mg L^{-1} [46]. The dissolution of F^-bearing minerals in alkaline water (7.1-8.9) like biotite, apatite, and muscovite present in these rocks may be responsible for a higher concentration of F^- in the groundwater. The geogenic sources of F^- (0.4-4.8 mg/L) in the Patan district of Gujrat are due to HCO_3^-, Na^+ and high pH in groundwater underlain by granite rocks [47]. The granites and pegmatites have been reported to release a high F in the Bastar zone in Chhattisgarh [48]. Since granite has a greater proportion of alkali and alkaline earth metals, it increases groundwater's pH suitable for the release of F^- from its precursor mineral [49].

A maximum concentration of F^- in pre-monsoon (7.2 mg/l) and post-monsoon (8.88 mg/l) duration has been reported in the Tamnar area of the Raigarh district of Chhattisgarh [50]. The plausible hydro-geochemical mechanism behind is the dissolution of feldspar and cation exchange, i.e., Na^+ with Ca^{2+} from the Gondwana supergroup of sandstones that releases F groundwater. Fluoride contamination (0.06-6.41 mg/l) has been reported in the Boden block of Orissa, surrounded by the eastern ghat group of formations comprising gneiss and granite charnockites, and khondalites [51]. $NaHCO_3$ alkalinity & higher pH was responsible for the leaching of the F^- from its minerals. Hydrological study in five villages of Sarguja district of Chhattisgarh having the geological formation of archean, gondwanas, lametas, and Deccan trap revealed maxi. 3.55 mg/l F^- in groundwater samples [52].

VI. CONCLUSION

Granite/ gneiss of archean eon during precambrian time have been present in almost all India's states where fluoride contamination has been detected. Sandstone, limestone, gypsum present in these rocks have good solubility in water, thus dissolving fluoride-bearing minerals present in them. High alkalinity in groundwater due to HCO3 ions also favors high fluoride ion concentration in groundwater. Na^+ has a positive correlation while Ca^{2+} shows a negative correlation with F^- & thus maintaining an equilibrium condition in groundwater.

Declaration

The authors declare that they have no conflict of interest.

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