THE MECHANISM OF FLUORINE REMOVAL BY CALCIUM SALTS—PART I

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The reaction between a sodium fluoride solution and calcium oxide, sulphate, carbonate, rock phosphate, fluorapatite and chlorapatite has been studied. It is shown (i) that rock phosphate, fluorapatite and chlorapatite do not enter into any reaction with the dissolved fluoride; (ii) that calcium oxide and sulphate remove fluorine from its aqueous solution by the mechanism of double decomposition, wherein the solubility of the precipitated calcium fluoride is the limiting factor for the complete removal of fluorine, and (iii) that calcium carbonate removes fluorine in the manner that can be mathematically denoted by the Freundlich adsorption isotherm. The peculiarities of the reaction between calcium carbonate and a solution of sodium fluoride are indicated.

INTRODUCTION

Two theories have been put forth to explain the removal of flourine from its aqueous solution by calcium salts, particularly the calcium salts of bone and other calcified structures. First one is the theory of anion exchange,[1, 2] and the second, of adsorption in terms of Freundlich adsorption isotherm.[3-5] As these theories stand, neither of these alone nor the combination of these both can explain satisfactorily the reaction between a dissolved fluoride and a calcium salt. Studies therefore have been carried out, employing different calcium salts, to elucidate the point in question, and the results obtained are presented here below.

PROCEDURE

Samples of calcium salts under investigation, weighing 1 gm., were shaken with fluorine solutions of different concentrations in glass stoppered bottles for a period ranging from few hours to few days. The period, for which the solutions were shaken, was arrived at after some preliminary experiments wherein the time required for the equilibrium between the solid and the liquid phase to be established, was noted. At the end of the shaking period, the solutions were filtered through filter No. 44, and the filtrate was analysed for sodium, fluorine, alkalinity and for the constituents of the adsorbent. Raw bone meal, purified bone meal, rock phosphate, chlorapatite, fluorapatite, calcium phosphate, oxide, carbonate and sulphate were the salts employed for the investigation. All the salts were finely powdered and passed through a 100-mesh sieve. The purified bone meal was prepared in the following manner: Chipped steamed bone meal, procured from the market, was coarsely powdered, and then treated with one per cent. alkali at 20 lb. pressure for half an hour. The autoclaved bone meal was then washed several times with water to remove excess alkali. The last traces of alkali were removed by passing carbon dioxide through a suspension of bone meal in water. The meal was finally washed with distilled water, dried at 100° C. and powdered. A sample of the purified bone meal was moistened with a little volume of water, and incubated at 37° C. for 48 hours. In case of putrefaction, the meal was autoclaved again with one per cent. alkali to make it free from putrifiable matter, and was finally washed. Chlorapatite, fluorapatite and rock phosphate were kindly supplied by the Geology Department of the Mysore Government. The other salts employed were of high grade purity. The composition of raw bone meal, purified bone meal, rock phosphate, chlorapatite fluorapatite and calcium phosphate is given in Table I.

TABLE I

Composition of raw bone meal, purified bone meal, rock phosphate, chlorapatite, fluorapatite and calcium phosphate

The results are expressed as percentages

	Nitrogen	Calcium	Phosphorus	Calcium Phosphorus	Magnesium	Carbonate	Fluoride
Raw bone meal ..	3·863	23·47	11·68	2·009	0·502	3·392	0·073
Purified bone meal	0·422	29·92	15·94	1·877	0·432	2·642	0·064
Rock phosphate ..	0·041	33·78	12·75	2·650	0·292	3·907	2·367
Chlorapatite ..	..	37·72	8·94	4·219	0·183	0·300	0·250
Fluorapatite ..	..	37·30	8·75	4·263	0·281	1·210	3·150
Calcium phosphate	..	31·91	15·96	1·999	..	..	..

The theoretical Ca: P ratio in $CaHPO_4$, $Ca(H_2PO_4)_2$ and $Ca_3(PO_4)_2$ is 1·29, 0·6452 and 1·936 respectively.

METHODS OF ANALYSIS

Fluorine was estimated by first converting it into hydrofluosilicic acid, and then titrating it with standard thorium nitrate solution in the presence of sodium alizarine sulphonate, (ii) phosphorus, by the method of Fiske and Subba Rao,[6] using the photoelectric colorimeter, (iii) calcium, by the method of permanganate titration, (iv) nitrogen, by Kjeldahl method, (v) carbonate, by the manometric method of Vanslyke and Folch,[7] (vi) sulphate, by precipitation with barium chloride, and (vii) sodium, with zinc-uranyl-acetate reagent according to the colorimetric method of Darnel and Walker,[8] and according to the gravimetric method of Barber and Kolthoff,[9] and magnesium was estimated as phosphate by the method of Denis.[10] For the determination of alkalinity in the filtrate, in the absence of salts, an aliquot was taken, and to this excess N/50 sulphuric acid was added. The excess sulphuric acid was determined by titration with N/50 alkali. In case of large salt concentration in the filtrate, the alkalinity, if possible, was determined potentiometrically.

RESULTS

The results, presented in the following tables, are about the reaction between a soluble fluoride and rock phosphate, chlorapatite, fluorapatite, calcium oxide, sulphate and carbonate only. The data about the reaction between a soluble fluoride and raw and purified bone meals and calcium phosphate are given in the second part. From the results presented in Tables II and III, it can be seen that the removal of fluorine by calcium oxide and calcium sulphate is effected by a simple process of double decomposition. In the first case, sodium hydroxide and insoluble calcium fluoride are formed, and in the second, sodium sulphate and calcium fluoride. In both cases, fluorine in the concentrations employed for these experiments, save for a trace, is removed entirely.

In Table IV are presented the data regarding the mode of reaction between calcium carbonate and sodium fluoride solution of different concentrations. It will be seen that, in the reaction between calcium carbonate and sodium fluoride solution, part of fluorine is removed from the solution. The clear filtrate has the same sodium concentration as the original solution, is highly alkaline, contains less fluorine and no calcium, and has the carbonate concentration equivalent to the quantity of fluorine removed. From the data given in Table IV, the following values have been calculated: (i) mgm. of fluorine removed per gm. of calcium carbonate, and (ii) the concentration of fluorine remaining in the solution at equilibrium. These values have been plotted logarithmically, and a straight line relationship has

TABLE II

Reaction between calcium oxide and sodium fluoride solution

No.	Composition of the solution in mg. per 100 c.c.		Composition of the clear supernatant in mg. per 100 c.c.			Alkalinity of the supernatant c.c. of N/50 NaOH	Alkalinity due to dissolved CaO (c.c. of N/50 NaOH)	Alkalinity due to NaOH formed (c.c. of N/50 NaOH)	Fluorine corresponding to the quantity of NaOH formed (calculated) mg.	Fluorine removed (observed) mg.
	Na	F	F	Na	Ca					
1	00·00 (Pure H_2O)	00·00	00·00	00·00	77·10	199·50	199·50	00·00	00·00	00·00
2	21·76	17·98	0·64	22·10	68·02	220·00	176·00	44·00	16·78	17·34
3	27·97	23·11	0·65	27·05	65·43	227·60	169·30	58·30	22·24	22·46
4	41·96	34·66	0·72	43·25	60·32	244·00	156·10	87·90	33·55	33·94
5	55·91	46·19	0·75	55·75	55·54	262·00	143·70	118·30	45·12	45·44
6	69·93	57·79	0·77	71·45	51·76	282·90	134·00	148·90	56·78	57·02
7	83·90	69·33	0·80	86·25	47·54	301·20	123·00	178·20	67·98	68·52

TABLE III

Reaction between calcium sulphate and sodium fluoride solution

No.	Composition of the solution in mg./100 c.c.		Composition of the clear supernatant in mg. per 100 c.c.				SO_4 due to dissolved $CaSO_4$ (mg. of $BaSO_4$)	SO_4 due to Na_2SO_4 formed (mg. of $BaSo_4$)	Fluorine corresponding to the quantity of sodium sulphate formed in mg. (calculated)	Fluorine removed in mg. (observed)
	Na	F	Na	F	Ca	SO_4 (in mg. of $BaSO_4$)				
1	00·00 (Pure H_2O)	00·00	00·00	00·00	61·86	374·00	374·00	00·00	00·00	00·00
2	21·76	17·98	22·04	0·52	56·08	438·00	327·20	110·80	18·03	17·46
3	27·97	23·11	27·05	0·52	54·36	455·10	317·20	137·90	22·45	22·59
4	41·96	34·66	43·10	0·61	51·66	518·10	301·40	216·70	35·27	34·05
5	55·91	46·19	55·95	0·65	48·11	558·60	280·60	278·00	45·25	45·54
6	69·93	57·79	71·60	0·74	45·20	612·70	263·70	349·00	56·82	57·05
7	83·90	69·33	86·10	0·93	42·58	663·40	248·40	415·00	67·54	68·40

been obtained (Fig. 1). It is seen that the mechanism of reaction between calcium carbonate and sodium fluoride solution can be mathematically denoted by the Freundlich adsorption equation, $x/m = kc^{1/n}$ or log x/m = log. $k + 1/n$ log c. Thus, it would seem that the removal of fluorine from its aqueous solution by calcium carbonate takes place by the process of adsorption, and not by a process of double decomposition such as takes place between calcium oxide or calcium sulphate and sodium fluoride solution. Such a reaction, in fact, cannot take place between calcium carbonate and sodium fluoride solution in view of the insolubility of the calcium carbonate in water. One litre of saturated solution of calcium carbonate in ordinary distilled water contains $19 \cdot 6 \times 10^{-5}$ gm. mols. of calcium carbonate.[11]

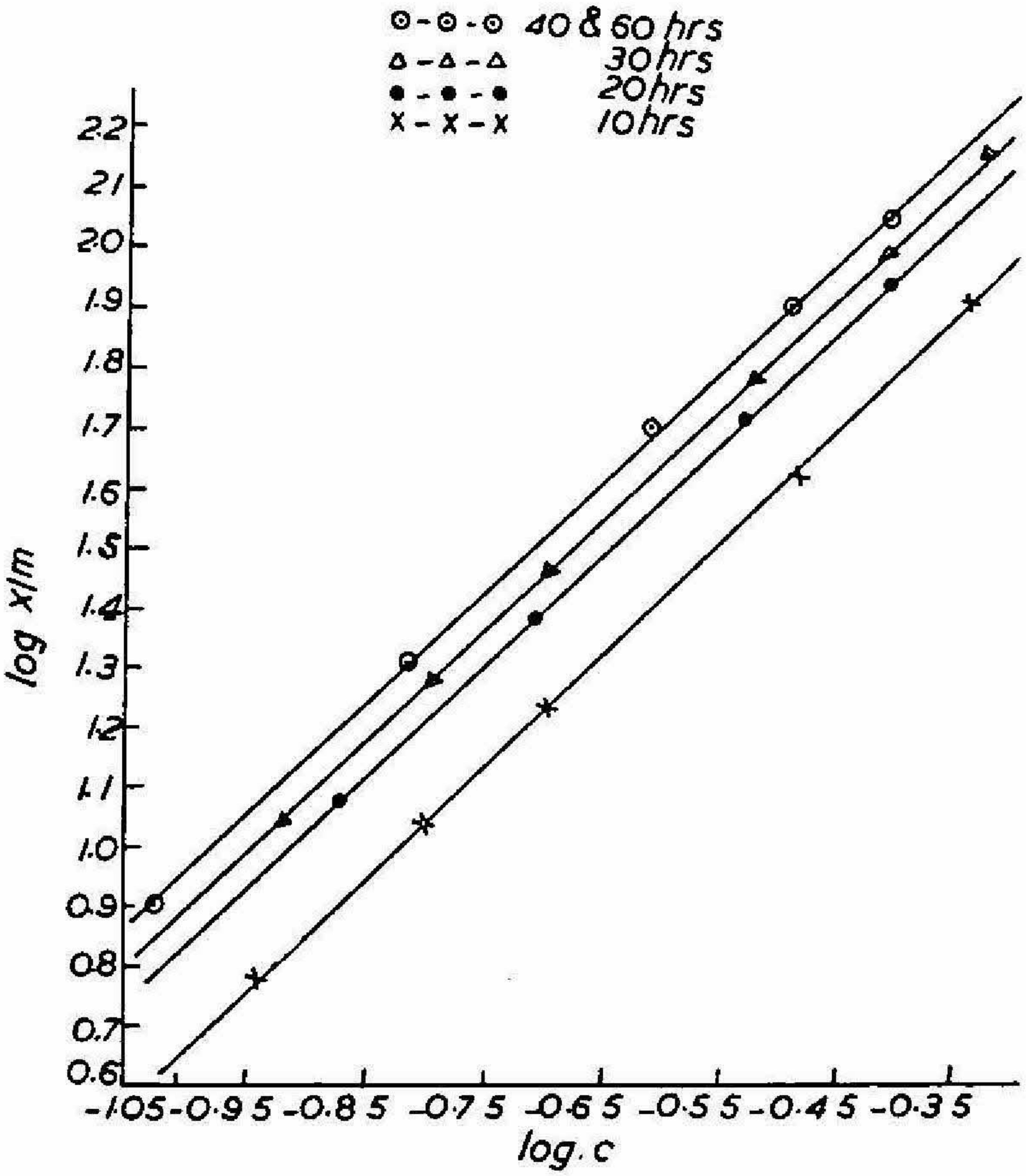

FIG. 1. Freundlich absorption isotherm curves for calcium carbonate and sodium fluoride solution at different time intervals

As the filtrate and the original solution have the same sodium concentration, the adsorption is not molecular but ionic, and as the filtrate contains carbonate in the equivalent concentration of fluorine removed, the reaction, though one of adsorption, involves the ionic exchange of

TABLE IV

Reaction between calcium carbonate and sodium fluoride solution

No.	Composition of the solution in mg. per 100 c.c.		Composition of the clear filtrate in mg. per 100 c.c.				Alkalinity (in terms of N/50 alkali) (c.c.)	Fluorine removed (mg.)	Ratio fluorine removed: CO_3 formed
	Na	F	Na	F	Ca	CO_3			
1	00·00	00·00	00·00	00·00	0·46	00·59	1·10	00·00	00·00
2	25·90	21·40	26·40	13·46	Nil	13·20	22·00	7·94	00·60
3	51·80	42·80	52·70	22·32	Nil	34·10	55·01	20·48	00·60
4	103·60	85·60	105·9	34·61	Nil	78·26	135·30	50·99	00·65
5	155·4	128·40	158·1	44·90	Nil	135·00	221·00	83·50	00·62
6	207·20	171·20	208·3	55·00	Nil	186·20	307·00	116·20	00·62
7	259·00	214·00	263·4	66·80	Nil	235·00	388·4	147·2	00·62

Calculated ratio = 0·63.

TABLE V

Reaction between rock phosphate, fluorapatite and sodium fluoride solution

No.	Composition of the solution in mg. per 100 c.c.			Composition of the clear filtrate in mg. per 100 c.c.				Alkalinity in terms of N/50 NaOH (c.c.)
	Na	F		Na	F	Ca	PO_4 as (P)	
1	00·00	00·00	Rock phosphate	00·51	1·20	0·70	Nil	6·50
			Fluorapatite	00·00	00·00	0·66	..	2·35
2	6·98	5·77	Rock phosphate	7·71	7·02	0·70	Nil	6·50
			Fluorapatite	7·12	5·50	0·66	..	3·35
3	13·96	11·54	Rock phosphate	15·12	12·92	0·72	Nil	6·93
			Fluorapatite	14·20	11·32	0·66	..	3·60
4	20·94	17·31	Rock phosphate	22·21	19·30	0·70	Nil	6·93
			Fluorapatite	21·57	17·30	0·64	..	3·60
5	27·92	23·08	Rock phosphate	30·00	25·14	0·69	Nil	6·70
			Fluorapatite	28·35	22·72	0·64	..	3·82
6	34·90	28·85	Rock phosphate	36·12	31·42	0·75	Nil	6·70
			Fluorapatite	33·90	28·08	0·62	..	3·82
7	41·88	34·62	Rock phospahte	43·75	37·54	0·73	Nil	6·93
			Fluorapatite	41·24	33·24	0·69	..	3·65

carbonate with fluoride in the molecule of calcium carbonate. Though the reaction between calcium carbonate and a dissolved fluoride seems to be one of ionic adsorption, it should, however, be noted that in any adsorption reaction though the quantity of the substance adsorbed per gm. of the material increases with the concentration of the substance in the solution, the percentage adsorption decreases with the increasing concentration of the substance in the solution. In the case of removal of fluorine by calcium carbonate, though the amount of fluorine removed per gm. of calcium carbonate has increased from 7·94 mgm. to 147·2 mgm., *i.e.*, 18·54 times, as the concentration of fluorine has been raised from 21·4 mgm. to 214 mgm. per 100 c.c., *i.e.*, 10 times, the percentage of fluorine removed per gm. of calcium carbonate has also increased from 37·10 to 68·80. This is not characteristic of any adsorption reaction.

In Table V are given the data on the manner of reaction between a sodium fluoride solution, and fluorapatite and rock phosphate. From the results presented, it is seen that fluorine is not removed when rock phosphate or fluorapatite is shaken with sodium fluoride solution of different concentrations. On the contrary, the filtrate in the case of rock phosphate contains more fluorine than the original solution. The soluble fluorides in rock phosphate can account for the excess fluorine in the filtrate. Similarly, chlorapatite has not shown any fluorine removing property. The suggestion of Smith and Davey[2] that the final removal of fluorine by treated bone meal may be accomplished by the displacement of chloride radical and the formation of fluorapatite is not confirmed at least in the natural chlorapatite.

The results are discussed in the second part of this piece of investigation.

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