THE MECHANISM OF FLUORINE REMOVAL BY CALCIUM SALTS—PART II

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Abstract

The removal of fluorine by raw bone-meal, purified bone-meal and calcium phosphate has been studied. It is shown that the removal of fluorine by raw bone-meal, purified bone-meal and calcium phosphate takes place in the manner of Freundlich adsorption isotherm. The adsorption of fluorine is shown to be ionic, involving the exchange of fluoride with the already adsorbed anions like hydroxide, carbonate and phosphate of these substances.

Introduction

In the first part,[1] the data have been presented on the mode of reaction between a solution of sodium fluoride and calcium oxide, sulphate, carbonate, rock phosphate, fluor-apatite and chlor-apatite. In this part, the results are given on the mode of reaction between a solution of sodium fluoride and raw bone-meal, purified bone-meal and calcium phosphate. The general procedure followed, and the methods of analysis employed are the same as described in the first part.

Results

The results are presented in Table I.

In Table I are given the data on the mode of reaction between raw bone-meal, purified bone-meal, calcium phosphate and sodium fluoride solution. In the reaction between bone-meals and sodium fluoride solution, the liquid phase at equilibrium was found to be alkaline, and was found to contain carbonate and phosphate. As certain peculiar difficulties were encountered in the accurate estimation of carbonate, the data on the presence of carbonate in the liquid phase are not included in Table I. Its presence in the liquid phase is covered by the determination of the total alkalinity of the liquid phase. From the results presented, it is noticed that (i) the clear filtrate, in every case, has the same sodium concentration as the original solution; (ii) the filtrate is alkaline, contains phosphorus and small quantities of calcium; (iii) the fluorine concentration of the filtrate is less than that of the original solution, indicating that fluorine is removed by these substances. When the logarithm of the quantity of fluorine removed per gm. of the substance is plotted against the logarithm of the concentration of fluorine remaining in the solution at equilibrium, a straight line relationship is obtained in each case (Fig. 1), indicating that the removal of fluorine by these substances is brought about by the mechanism of adsorption. This is supported by the observation that the quantity of fluorine,

TABLE I

Reaction between raw bone-meal, purified bone-meal, calcium phosphate and sodium fluoride solution

	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 sodium hydroxide* (c.c.)
	Na	F (*a*)		Na	F (*b*)	Ca	PO_4 as (P)	
1	00·00	00·00	RBM	00·00	00·00	2·65	0·34	19·50
			PBM	00·00	00·00	0·35	00·00	8·64
			CP	00·00	00·00	0·36	0·39	2·06
2	10·35	8·54	RBM	10·75	0·45	0·38	1·96	25·84
			PBM	10·70	4·59	0·18	0·77	11·41
			CP	10·85	6·20	0·24	1·12	4·91
3	21·76	17·98	RBM	22·21	8·55	0·20	2·88	27·11
			PBM	21·54	13·49	0·14	1·72	12·05
			CP	22·12	14·44	0·20	1·47	6·26
4	28·04	23·17	RBM	29·57	12·62	0·20	3·69	27·90
			PBM	29·57	17·26	0·18	2·06	14·58
			CP	28·97	19·15	0·20	1·79	6·81
5	50·98	42·12	RBM	52·12	26·84	0·20	6·30	30·34
			PBM	50·54	33·12	0·18	3·35	15·90
			CP	51·98	35·65	0·15	2·71	7·13
6	76·45	63·18	RBM	79·21	42·55	0·18	8·76	31·95
			PBM	78·75	52·34	0·14	4·73	16·75
			CP	77·12	54·76	0·15	3·59	8·48
7	102·00	84·24	RBM	104·20	59·40	0·18	11·18	33·30
			PBM	100·90	70·60	0·09	5·83	17·45
			CP	101·00	74·84	0·09	4·51	9·19
8	127·50	105·30	RBM	130·20	77·51	0·20	13·69	34·45
			PBM	130·20	88·88	0·09	7·00	18·65
			CP	129·90	93·35	0·11	5·24	9·75

TABLE I—*Continued*

Reaction between raw bone-meal, purified bone-meal, calcium phosphate and sodium fluoride solution

No.		F removed $(a-b)$ (mgm.)	Alkalinity due to the reaction NaF NaOH (Total alkalinity *minus* alkalinity in the blank) (c.c.)	F removed as a result of this reaction (mgm.)	Remaining F (mgm.)	Ratio, Remaining F : PO_4 as (P) (Total phosphate *minus* phosphate in the blank) 3 F : P	Total F corresponding to OH^- and $PO_4^{\equiv}$ in the filtrate			Fluorine removed (observed) (mgm.)
							F corresponding to OH^-	+ $PO_4^{\equiv}$	Total (Calc.)	
1	RBM	00·00	00·00	00·00	00·00	00·00	..	..	..	..
	PBM	00·00	00·00	00·00	00·00	00·00	..	..	..	..
	CP	00·00	00·00	00·00	00·00	00·00	..	..	..	..
2	RBM	8·09	6·34	2·41	5·68	3·50	2·41	2·98	5·39	8·09
	PBM	3·95	2·77	1·05	2·90	3·77	1·05	1·41	2·46	3·95
	CP	2·34	2·85	1·08	1·26	1·72	1·08	1·34	2·42	2·34
3	RBM	9·43	7·61	2·89	6·54	2·57	2·89	4·67	7·55	9·83
	PBM	4·49	3·41	1·29	3·20	1·86	1·29	3·16	4·45	4·49
	CP	3·54	4·20	1·58	1·96	1·81	1·58	1·99	3·57	3·54
4	RBM	10·55	8·40	3·19	7·36	2·19	3·19	6·16	9·35	10·55
	PBM	5·91	5·94	2·25	3·66	1·77	2·25	3·80	6·05	5·91
	CP	4·02	4·75	1·80	2·22	1·59	1·80	2·57	4·37	4·02
5	RBM	15·28	10·84	4·12	11·16	1·87	4·12	10·96	15·08	15·28
	PBM	9·00	7·26	2·76	6·24	1·86	2·76	6·16	8·92	9·00
	CP	6·47	5·07	1·93	4·54	1·96	1·93	4·26	6·19	6·47
6	RBM	20·63	12·45	4·73	15·90	1·88	4·73	15·49	20·22	20·63
	PBM	10·84	8·11	3·08	7·76	1·64	3·08	8·71	11·79	10·84
	CP	8·42	6·42	2·43	5·99	1·87	2·43	5·89	8·32	8·42
7	RBM	24·84	13·80	5·24	19·60	[illegible]	5·24	19·97	25·21	24·84
	PBM	13·64	8·81	3·35	10·29	1·74	3·35	10·72	14·07	13·64
	CP	9·40	7·13	2·71	6·69	1·62	2·71	7·58	10·29	9·40
8	RBM	27·79	14·95	5·68	22·11	[illegible]	5·68	24·57	30·25	27·79
	PBM	16·42	10·01	3·80	12·62	[illegible]	3·80	12·87	16·67	16·42
	CP	11·95	7·09	2·92	9·03	1·86	2·92	8·91	11·83	11·95

RBM – Raw bone-meal; **PBM** – Purified bone-meal; **CP** – Calcium phosphate.

* Alkalinity referred to is total alkalinity *minus* alkalinity due to sodium phosphate formed.

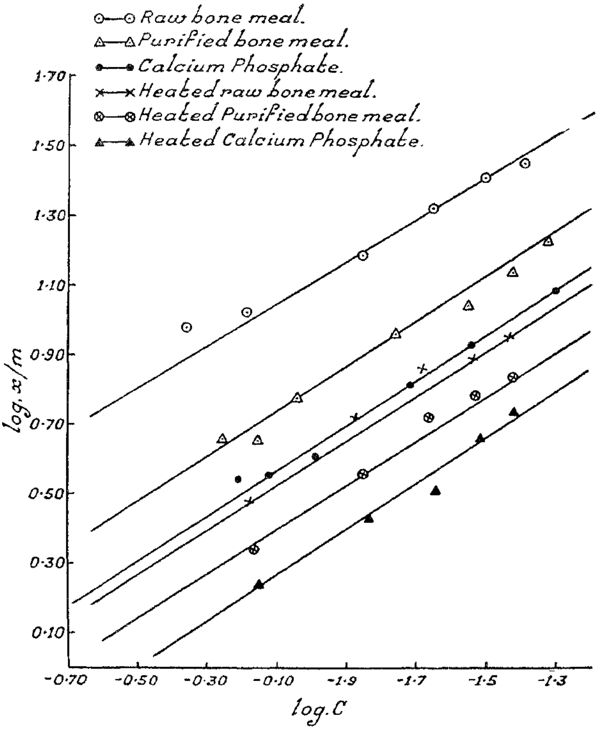

FIG. 1. Freundlich adsorption isotherm curves for equilibria between raw bone-meal, ed bone-meal, calcium phosphate, the corresponding heated products and sodium fluor de ion.

rbed per gm. of the material increases with the concentration of fluorine in solution, and with the period of contact between sodium fluoride solution and solid substances till equilibrium conditions are established (Fig. 2). As the inal solution and the filtrate have the same sodium concentration, and as the oval of fluorine in each case is followed by the production of phosphates and linity in the filtrate, it is adduced that the adsorption of fluorine is an instance mic adsorption, involving the exchange of fluorine with the adsorbed anions

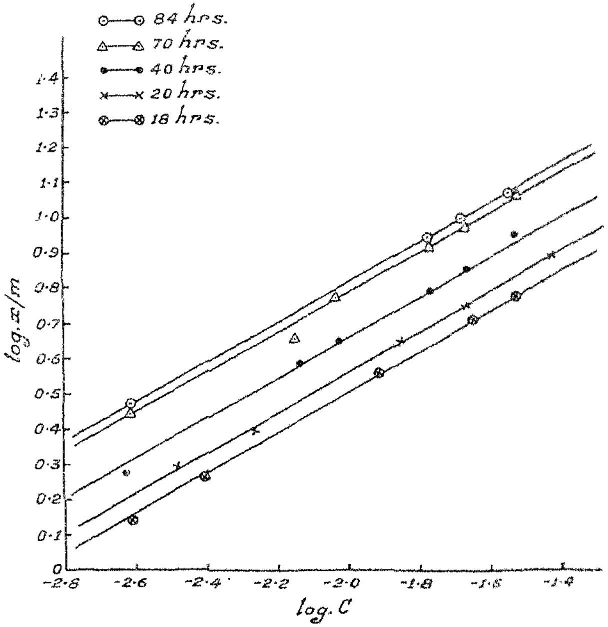

FIG. 2. Freundlich adsorption isotherm curves for purified bone-meal and sodium fluoride solution at different time intervals.

on the solid substance. It will therefore be necessary to explain ionic adsorption, to assume that bone salt and calcium phosphate have, on their surface, already adsorbed groups, acquired during the period and process of formation. Ordinarily, it would be a simple matter to prove, by ordinary methods of analysis, whether a particular compound is pure, or has got, on its surface, certain adsorbed groups, provided the constitution of the compound is firmly established. The constitution of bone salt and calcium phosphate is not definitely known. Based on their X-ray diffraction studies on calcium phosphates, Hodge and his associates[2] postulated that commercial tertiary calcium phosphates are probably hydroxy-apatite with more or less adsorbed phosphate ions to give empirical formulæ approaching the theoretical. Manly and Levy,[3] and Hodge and associates,[4] using the radioactive isotope, found that enamel, dentine, bone and hydroxy-apatite, when exposed to the solution of sodium phosphate, adsorb phosphate. Thus, it should not be considered irrelevant to assume that bone salt and calcium phosphate have certian adsorbed anions.

It has been assumed that the production of alkalinity in the filtrate is due to the ionic adsorption of fluorine, involving, in the case of calcium phosphate, the exchange of already adsorbed hydroxide with fluoride ion, resulting in the formation of sodium hydroxide, and involving, in the case of bone salt, the exchange of already adsorbed hydroxide and carbonate with fluoride ion resulting in the formation of sodium hydroxide and carbonate. Based on this assumption, the quantity of fluorine removed by exchange with the adsorbed hydroxide and carbonate is calculated from the alkalinity of the filtrate, employing the factor, 1 c.c. of N/50 alkali is equal to

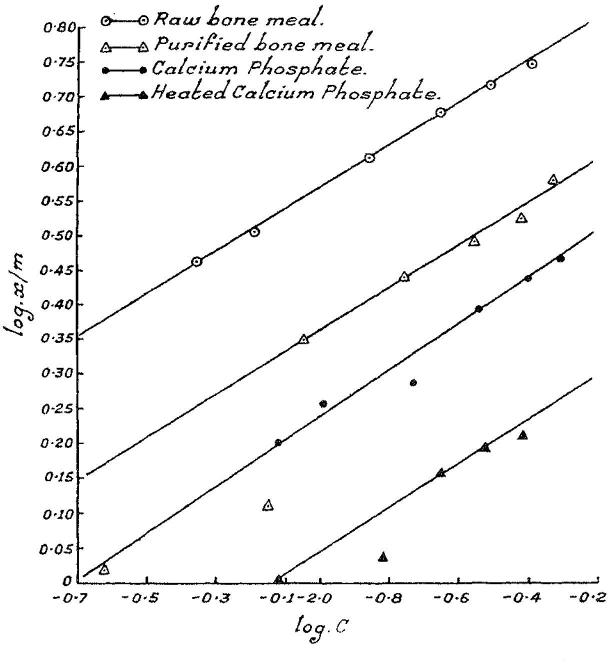

FIG. 3. Freundlich adsorption isotherm curves for equilibria between raw bone-meal, purified bone-meal, calcium phosphate, heated calcium phosphate and sodium fluoride solution (for explanation, *vide* data given in Tables I & III and the comments thereon).

0·38 mgm. of fluorine. The alkalinity of the filtrate referred to is the total alkalinity of the fitrate *minus* the alkalinity due to the sodium phosphate formed. For one mgm. of phosphorus, 2·75 c.c. of N/50 sodium hydroxide have been deducted. This figure for the alkalinity of sodium phosphate was obtained by determining the alkalinity of sodium phosphate solution of known concentration. The logarithm of the calculated value has been plotted against the logarithm of the concentration of fluorine in the filtrate at equilibrium.

Straight line relationship has been obtained in each case (Fig. 3). The calculated value of fluorine, removed by exchange with the adsorbed hydroxyl (and also carbonate in the case of bone salt), has been deducted from the observed value of total fluorine removed. The logarithm of the remaining fluorine removed has been

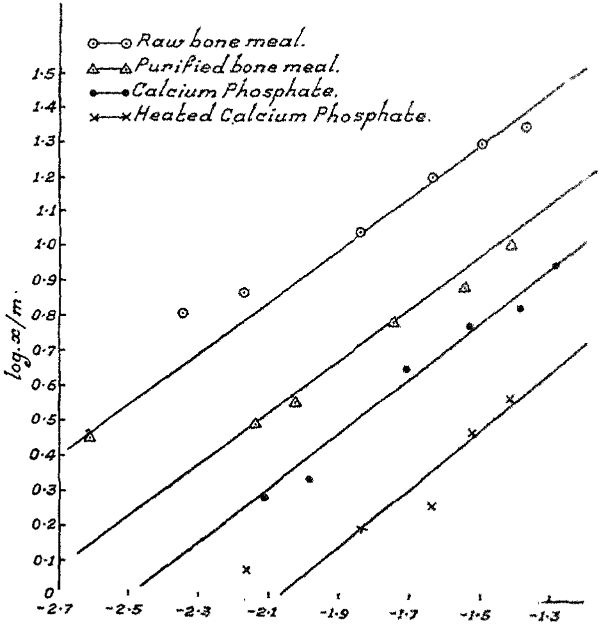

FIG. 4. Freundlich adsorption isotherm curves for equilibria between raw bone-meal, purified bone-meal, calcium phosphate, heated calcium phosphate and sodium fluoride solution (for explanation, *vide* data given in Tables I & III and the comments thereon).

plotted against the logarithm of the concentration of fluorine in the filtrate at euqilibrium. Straight line relationship has been obtained in this case also (Fig. 4).

The ratio of remaining fluorine adsorbed to phosphate, present in the filtrate, has been calculated. The ratio varies from 1·59 to 3·770. If it is assumed that the remaining adsorbed fluorine is removed by exchange with adsorbed phosphorus, the ratio, fluorine to phosphorus, 3 F^- : PO_4^- = 57/31, will be 1·839. Though there is considerable variation in the observed values of the ratio, F : P, it may be mentioned that this wide variation either represents some unkown course of reaction or it arises from the error involved in the determination of fluorine. To prove that

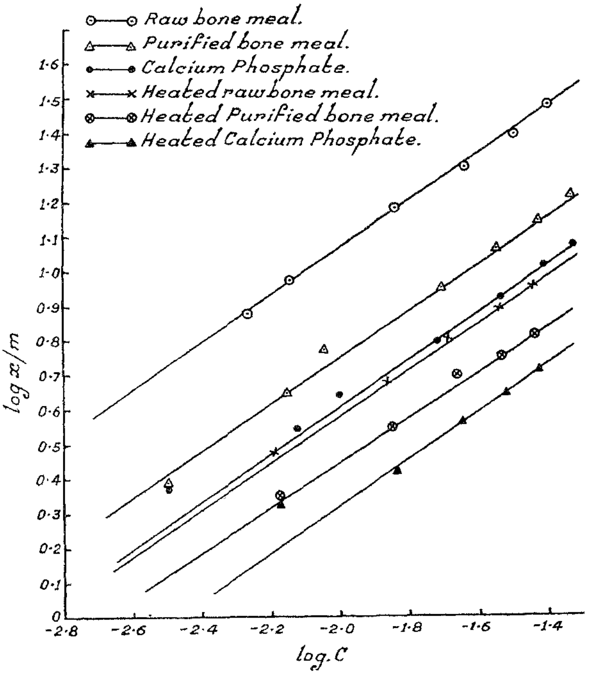

FIG. 5. Freundlich adsorption isotherm curves for calculated equilibria between raw bone-meal, purified bone-meal, calcium phosphate, the corresponding heated products and sodium fluoride solution.

the variation in the observed values is due very likely to the inaccuracies in the method of estimation of fluorine, it has been assumed that the alkalinity and the phosphate in the filtrate have been determined more accurately than fluorine, and that the removal of fluorine takes place partly by exchange with the adsorbed hydroxide (and also carbonate in the case of bone salt), and partly by exchange with adsorbed phosphate, and the total quantity of fluorine removed is the sum of fluorine removed by these two reactions. The total quantity of fluorine removed has been calculated from the alkalinity and phosphate concentration of the filtrate by using the factors, one c.c. of N/50 alkali = 0·38 mgm. of fluorine, and one mgm. of phosphate = 1·839 mgm. of fluorine. The calculated quantity of fluorine removed is subtracted from the total quantity of fluorine in the original solution. The value, thus obtained, is regarded as that of the concentration of fluorine in the solution at equilibrium. The logarithm of the calculated quantity of fluorine removed has been plotted against the logarithm of the fluorine concentration at equilibrium (Fig. 5). It is seen that, in this case, more plotted points lie on a straight line than in the case of observed values of fluorine removed, and at equilibrium. Thus, the assumption has been more or less experimentally proved that bone salt and calcium phosphates are not pure compounds, but have, on their surfaces, already adsorbed anions like hydroxide, carbonate and phosphate. In probability, the further adsorption of phosphates by these compounds takes place by the mechanism of ionic adsorption, involving the exchange of already adsorbed hydroxide or carbonate with phosphate. Fluorine, in part, replaces the adsorbed hydroxide and carbonate, and in part, the adsorbed phosphate. To separate that part of fluorine, which replaces the hydroxide and carbonate, from the part, which replaces the phosphate, or to so modify the compound that the removal of fluoride takes place by either of these reactions only would naturally be a step further in the experimental verification of the above hypothesis. Various methods have been tried to achieve this end, and the one, that has been found useful, is that requiring the heating of the compound at 500° C. in a muffle furnace for about 30 min. Raw bone-meal, purified bone-meal and calcium phosphate were heated in a muffle furnace for 30 min. The compounds were analysed before and after heating. The data are given in Table II.

It will be seen that the calcium: phosphorus ratio is the same after heating as before it, indicating that no loss of phosphorus has taken place during the course of heating, and that the change, if any, in the adsorptive properties of the compounds is not due to the loss of the mineral complement of the compound but due to the change in its essential structure.

The heated compounds were shaken with sodium fluoride solution of different concentrations, and the results obtained are presented in Table III.

It will be seen that, in the case of raw bone-meal and purified bone-meal, the filtrate does not contain any phosphorus but is highly alkaline. What changes the bone salt has undergone during the course of heating is difficult to say in the absence of data regarding the initial constitution of bone salt. From the loss in

TABLE II

Effect of heating at 500° C. on the composition of raw bone-meal, purified bone-meal and calcium phosphate

		Period of heating (min.)	Percentage loss in weight	Percentage phosphorus after heating	Percentage phosphorus corrected for percentage loss in weight
1.	Raw bone-meal ..	15	30·14	16·72	11·68
	Purified bone-meal ..	15	2·56	16·39	15·97
	Calcium phosphate ..	15	1·80	16·30	16·01
2.	Raw bone-meal ..	30	30·58	16·75	11·62
	Purified bone-meal ..	30	2·62	16·32	15·96
	Calcium phosphate ..	30	1·94	16·35	16·03
3.	Raw bone-meal ..	45	30·61	16·82	11·67
	Purified bone-meal ..	45	2·70	16·92	16·46
	Calcium phosphate ..	45	2·10	16·42	16·07
4.	Raw bone-meal ..	60	30·81	16·45	11·38
	Purified bone-meal ..	60	2·70	16·75	16·29
	Calcium phosphate ..	60	2·12	16·52	16·17
5.	Raw bone-meal ..	75	30·54	16·56	11·24
	Purified bone-meal ..	75	2·92	16·21	15·76
	Calcium phosphate ..	75	2·22	16·55	16·78

Percentage phosphorus in unheated samples:

Raw bone-meal ..	11·68
Purified bone-meal .	15·94
Calcium phosphate ..	15·97

weight, and no loss in the mineral complement of the bone, it may be inferred that the reaction must be intramolecular, taking place inside the compound itself. According to Hodge and associates,[2] when calcium phosphate is precipitated from the solution rich in phosphate, many multipolar phosphate ions are drawn around the tiny crystals, and the precipitate consequently contains an excess of phosphate. Upon ignition, there may be a reaction between the excess phosphate and the crystal of hydroxyl apatite, producing the β-$Ca_3P_2O_8$ in amounts, limited only by the amount of excess phosphate.

The filtrate from heated calcium phosphate contains phosphate, and is alkaline. It will be observed that fluorine has been adsorbed by all the three heated compounds. As the filtrate and the original solution have the same sodium concentrations, the adsorption of fluorine is ionic, involving the exchange of fluorine

TABLE III

Reaction between heated raw bone-meal, purified bone-meal, calcium phosphate and sodium fluoride solution

No.	Composition of the solution in mgm. per 100 c.c.			Composition of the clear filtrate in mgm. per 100 c.c.				Alkalinity in terms of N/50 NaOH (c.c.)
	Na	F(*a*)		Na	F(*b*)	Ca	PO_4 as (P)	
1	00·00 (Pure H_2O)	00·00	HRBM HPBM HCP	00·00 00·00 60·00	00·00 00·00 00·00	2·42 1·01 0·56	00·00 00·00 1·78	4·58 3·72 2·30
2	18·26	15·08	HRBM HPBM HCP	18·10 18·45 18·50	11·58 13·14 12·58	0·39 0·22 0·22	00·00 00·00 2·70	12·53 9·62 4·91
3	36·52	30·16	HRBM HPBM HCP	37·21 37·10 37·42	24·96 26·57 27·47	0·21 0·21 0·25	00·00 00·00 2·92	17·17 13·17 5·15
4	54·78	45·24	HRBM HPBM HCP	55·92 55·90 55·40	38·14 [illegible] 42·00	0·20 0·15 0·17	00·00 00·00 3·16	21·57 16·80 6·02
5	73·08	60·32	HRBM HPBM HCP	73·10 74·78 74·45	52·60 54·47 55·54	0·20 0·20 0·15	00·00 00·00 3·39	25·01 18·41 6·34
6	91·30	75·40	HRBM HPBM HCP	90·70 92·74 92·72	56·20 [illegible] 70·03	0·15 0·15 0·20	00·00 00·00 3·31	[illegible] [illegible] [illegible]

HRBM = Heated raw bone-meal; HPMB = Heated purified bone-meal; HCP = Heated calcium phosphate.

TABLE III—*Continued*

Reaction between heated raw bone-meal, purified bone-meal, calcium phosphate and sodium fluoride solution

No.	F removed $(a-b)$ (mgm.)	Alkalinity due to the reaction NaF NaOH (Total alkalinity *minus* alkalinity in the blank) (c.c.)	F removed as a result of this reaction (mgm.)	Remaining F (mgm.)	Ratio. Remaining F : PO_4 as (P). (Total phosphate *minus* phosphate in the blank)	Total F corresponding to OH^- and $PO_4^{\equiv}$ in the filtrate			Fluorine removed (observed mgm.)
						F corresponding to OH^-	+ $PO_4^{\equiv}$	= Total (Calc.)	
1 HRBM	00·00	00·00	00·00	00·00	..	..	..	..	
HPBM	00·00	00·00	00·00	00·00	..	..	..	..	
HCP	00·00	00·00	00·00	00·00	..	..	..	..	
2 HRBM	3·50	7·95	3·02	0·48	..	3·02	00·00	3·02	3·50
HPBM	1·74	5·0	2·24	−0·50	..	2·24	00·00	2·24	1·74
HCP	2·20	2·61	1·00	1·20	1·30	1·00	1·69	2·69	2·20
3 HRBM	5·20	12·59	4·78	0·42	..	4·78	00·00	4·78	5·20
HPBM	3·59	2·45	3·60	−0·01	..	3·60	00·00	3·60	3·59
HCP	2·69	2·85	1·08	1·61	1·41	1·08	2·09	2·17	2·69
4 HRBM	7·10	16·99	6·45	0·65	..	6·45	00·00	6·45	7·10
HPBM	5·14	13·08	4·97	0·17	..	4·97	00·00	4·97	5·14
HCP	3·24	3·72	1·41	1·83	1·32	1·41	2·53	3·94	3·24
5 HRBM	7·72	20·43	7·76	−0·04	..	7·76	00·00	7·76	7·72
HPBM	5·87	14·68	5·58	0·29	..	5·58	00·00	5·58	5·87
HCP	4·48	4·04	1·53	2·95	1·83	1·53	2·96	4·49	4·48
6 HRBM	8·50	23·45	8·91	−0·41	..	8·91	00·00	8·91	8·50
HPBM	6·72	17·03	6·47	0·25	..	6·47	00·00	6·47	6·72
HCP	5·37	4·20	1·60	3·77	1·95	1·60	3·55	5·15	5·37

HRBM = Heated raw bone-meal; HPBM = Heated purified bone-meal; HCP = Heated calcium phosphate.

with the adsorbed hydroxide, and carbonate in the case of raw and purified bone-meal, and with the adsorbed hydroxide and phosphate in the case of calcium phosphate. The quantity of fluroine adsorbed in each case has been calculated from the alkalinity and phosphate concentration of the filtrate in the manner indicated above, and the calculated values have been, similarly, logarithmically, plotted against the calculated values of fluorine at equilibrium. As with unheated compounds (Fig. 5), so with the heated ones, more points have been found to lie on a straight line than in the case of observed values. Thus, by this additional evidence, it is further proved that the adsorption of fluorine by raw bone-meal, purified bone-meal and calcium phosphate involves the replacement of the adsorbed anions like hydroxide, carbonate and phosphate with fluorine, and that, on heating the [illegible] at 500° C for half an hour, the adsorption of fluorine, in the case of raw and purified bone-meal, takes place by the replacement of adsorbed hydroxide and carbonate alone.

From the results presented in the foregoing tables, it has been observed that, in no case, sodium from sodium fluoride solution has been adsorbed by raw bone-meal, purified bone-meal and calcium phosphate. This is in direct contrast to the findings of Hodge and his associates,[9] who observed that, when exposed to

TABLE IV

Sodium concentration in the beginning and at the end of the reaction

No.	Sodium in mgm. per 100 c.c. of the original solution		Sodium in mgm. per 100 c.c. of the filtrate
1	209·00	RBM	211·3
		PBM	213·0
		CP	211·3
2	418·00	RBM	430·1
		PBM	426·0
		CP	427·0
3	627·00	RBM	640·1
		PBM	635·0
		CP	637·2
4	836·00	RBM	843·2
		PBM	836·8
		CP	843·2
5	1045·00	RBM	1022·0
		PBM	1025·0
		CP	1035·0

RBM = **Raw bone-meal**; **PBM** = **Purified bone-meal**; **CP** = **Calcium phosphate.**

solutions of sodium chloride, containing the radioactive isotope Na^{24}, samples of powdered apatite, bone, dentine and enamel picked up sodium in a manner that could be expressed by the Freundlich adsorption equation. It was thought that this disagreement in the results might be due to the fact that comparatively more dilute solutions of sodium, and less accurate methods for the estimation of sodium, have been employed in this case than those employed by Hodge and his associates. Radioactive sodium was estimated by Hodge by the usual Geiger Counter method, whereas sodium, in this case, was estimated either colorimetrically or gravimetrically, in both cases, precipitating sodium with zinc-uranium-acetate reagent. Bearing this in mind, larger concentrations of sodium fluoride were employed for studying the reaction between sodium fluoride solution and bone-meals and calcium phosphate, and sodium was estimated gravimetrically.

The values of sodium in the beginning and at the end of the reaction from one set of experiments are given in Table IV.

It will be seen that there is some scatter in the values of sodium at the end of the reaction. Bearing in mind that not more than 7 mgm. of sodium can be estimated by the method employed, the variation in the results is not regarded of any significance. The smallness of the quantity of sodium that can be estimated accurately, will necessitate the employment of a very small aliquot of the filtrate for sodium estimation, and any error in the actual estimation of sodium, in the final computation of the results, will be multiplied by 100 or even by 200 times. The conclusions already arrived at therefore stand further confirmed.

Discussion

Calcium oxide and calcium sulphate remove fluorine from aqueous solution by the process of double decomposition between the dissolved sulphate or oxide and the soluble fluoride. For the complete removal of fluorine by such procedure, the solubility of the precipitated calcium fluoride is the limiting factor. Rock phosphate, chlorapatite and fluorapatite, in spite of being akin to calcium phosphate and bone salt in the placement of principal molecular lattices, do not show any fluorine removing property. When present in very small concentrations, fluorine is not removed by calcium carbonate. However, calcium carbonate does remove fluorine from its aqueous solution, when it is present in sufficiently large concentration, in a manner that, approximately, can be mathematically expressed by the Freundlich adsorption isotherm, such an adsorption of fluorine by calcium carbonate differs from any normal adsorption in the following ways: (i) the adsorption does not take place when fluorine is present in very low concentration; (ii) the percentage of fluorine adsorbed increases with the increasing concentration of fluorine.

Raw bone-meal, purified bone-meal and calcium phosphate remove fluorine, from its aqueous solution, by the process of ionic adsorption, involving the exchange of fluorine with the anions like hydroxide, carbonate and phosphate. The concentration of sodium in all cases has been found to be the same in the solution before and after adsorption. Hodge and associates,[3] working on the nature of the insoluble sodium of bone, and with radioactive sodium, found that sodium was adsorbed by bone, hydroxy apatite, dentine and enamel, and that bone, which *in vivo*, contains about 2 mgm. of sodium per gm., is capable of taking about 7 times this quantity from a 3 M sodium chloride solution. Explaining the mechanism of adsorption of sodium by bone, the authors first suggested the following two mechanisms: (i) Na^{23} marked with Na^{24} exchanges with Na^{23} or with other cations or Na^{24} preferentially exchanges with Na^{23}, and thus gives a false rate of Na^{23} turnover or (ii) sodium as sodium chloride is adsorbed as a molecule. According to the authors, the first mechanism was not likely to take place, and to investigate the possibility of the occurrence of the second, enamel samples, before and after exposure to 3 M sodium chloride solution, were analysed for chloride content. Before exposure, the enamel samples contained 0·045 mgm. of chloride per 100 mgm. of the sample. After exposure, the samples contained 0·331 mgm. of chloride per 100 mgm. of the sample. The increase, after exposure, corresponds to about 2·8 mgm. of chloride per gm. of enamel, which, as sodium chloride, would be accompanied by 1·8 mgm. of sodium. Enamel, under these conditions, has taken up about 14 mgm. of sodium per gm. The adsorption of molecular sodium chloride can account for only one-eighth of the total, *i.e.*, nearly the amount (2 mgm. of sodium per gm. of bone) usually present in the bone *in vivo*. In consequence the authors suggested that the exchange of sodium from solution with other cations of the calcified tissues might be the mechanism of adsorption of sodium. However, no evidence has been presented to support this hypothesis, nor, sodium, in the present case, has been found to be adsorbed from a solution of sodium fluoride by raw or purified bone-meal, calcium phosphates, rock phosphate, fluor- and chlor-apatites.

One fact that emerges clear from the results presented, is that the bone salt and calcium phosphate have adsorbed anions like hydroxide, carbonate and phosphate. This is partially supported by the X-ray diffraction studies of Hodge and associates[2] on the constitution of tertiary calcium phosphates. According to them, the commercial tertiary calcium phosphates are probably hydroxyl apatites with more or less adsorbed phosphate ions, resulting in empirical formulæ, approaching the theoretical values for calcium phosphate. The observation of Gabriel,[6] confirmed by Logan,[7] that bone, wet ashed, contains an excess of 6 per cent. basic over acidic equivalents, can be explained on the basis of bone possessing adsorbed hydroxide. Bone salt and calcium phosphate can thus be expected to equilibrate the concentration of adsorbed anions with the concentration of these or other anions in the surrounding medium. Such a behaviour has been recorded for calcium phosphate *in vitro*,[8] and for bone salt *in vivo*.[9-12] Thus, it may be stated that bone salt or calcium phosphate is not a single chemical entity. The bone salt seems to be composed of two parts: the one, that is in immediate equilibrium with the body fluids, and whose composition is determined by the composition of the liquid phase, may be termed the labile part; and the other, which is relatively much less affected by the composition of the liquid phase, may be termed the non-labile part. The labile part of the bone has the adsorbed hydroxide, carbonate and phosphate, and probably other anions, and according to Hodge and associates,[5] also adsorbed cations like sodium.

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REFERENCES

1. Wadhwani, T. K. .. *J. Ind. Inst. Sci.*, 1954, **36**, 250.
2. Hodge, H. C., LeFevre, M. L. and Bale, W. F. *Ind Eng. Chem. Anal. Ed.*, 1938, **10**, 156.
3. Manly, M. L. and Levy, S. R. *J. Am. Chem. Soc.*, 1939, **61**, 2588.
4. Hodge, H. C., Van Huysen, G., Bonner, J. F. and Van Voorhis, S. N. *J. Biol. Chem.*, 1941, **138**, 451.
5. ——— and Associates *Ibid.*, 1943, **148**, 321.
6. Gabriel, S. .. *Ztschr. Physiol. Chem.*, 1894, **18**, 257.
7. Logan, M. A. .. *J. Biol Chem.*, 1935, **110**, 375.
8. ——— and Taylor, H. L. *Ibid.*, 1938, **125**, 377.
9. Chiewitz, O. and Hevesy, G. *Nature*, 1935, **136**, 754.
10. Hahn, L. A., Hevesy, G. and Lundsgaard, E. C. *Biochem., J.* 1937, **31**, 1705.
11. Manly, M. L. and Bale, W. F. *J. Biol. Chem.*, 1939, **129**, 125.
12. Hevesy, G. and Armstrong, W. D. *Ibid.*, 1940, **133**, 44.