FLUORIDES IN SOIL

Behavior of Incorporations of Potassium and Calcium Fluorides in a 6-Year Lysimeter Study

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Incorporations of calcium and potassium fluorides were compared, with and without limestone or fused wollastonite, in a 6-year lysimeter experiment. Wollastonite alone caused increases in fluorine outgo beyond the amounts the soils received from rain waters. Fluorine recoveries from coarse and fine slag were 6 and 10% in Hartsells sandy loam and 20 and 34% in Clarksville silt loam. Recoveries of fluorine from calcium fluoride in both unlimed soils exceeded the corresponding recoveries from potassium fluoride. The mean for the five total recoveries of fluorine from potassium fluoride was 6.6% for Hartsells and 10.6% for Clarksville, against the corresponding potassium recoveries of 44.6 and 60.2%. Both soils retained the entire potassium content of the slag incorporations. In 28 comparisons, added calcium lessened the leachings of potassium, whereas added potassium caused decreases in outgo of calcium and magnesium. In general, wollastonite was more effective than limestone in causing outgo of fluorine and was less repressive upon outgo of potassium and magnesium.

Additive fluorine was virtually ignored as a factor in soil and plant chemistry until 1934, when significance was attached to the possibility that the calcium fluoride carried by superphosphate incorporations might induce soil reactions and influence the fluorine content of vegetation. Hart, Phillips, and Bohstedt (*2*) then suggested that cumulative incorporations of phosphatic fertilizers might cause forage crops to acquire fluorine contents that would prove injurious in the grazing and feeding of livestock. However, their analyses of samples of forage vegetation from phosphated soils at several experiment stations did not register increases in fluorine content. In a later pot culture experiment at the Tennessee Experiment Station, nine successive crops failed to show increases in fluorine uptake from a heavy-rate single incorporation of 18% superphosphate. That incorporation provided the amount of fluorine that would be carried by 448 annual incorporations of $^1/_4$ ton of superphosphate. The effect of the acidity of the superphosphate, and of the monocalcium phosphate control, was ameliorated through a companion input of 100-mesh wollastonite (*12*).

However, it is important to distinguish between the behavior of the component fluoride of superphosphate and the corresponding fluoride formed when soluble fluorides are added to limed soil (*3*, *4*, *6*, *13*). The fluoride component of quenched calcium silicate slag has imparted a high concentration of fluorine to lysimeter leachings (*7*), presumably as calcium silicofluoride; yet such concentration in the free water of the soil does not cause increase in plant uptake of fluorine (*12*).

Although additions of potassium and calcium fluorides have not been compared directly in pot culture experiments or in lysimeter studies at this Tennessee station, the fluoride and the chloride of potassium were compared at three rates on two soils in pot cultures. The findings demonstrated selective fixation of the additive fluorine, with concomitant liberation of potassium and resultant elevation in soil pH and lethal effect upon plant growth by the 800-pound inputs, in both soils (*10*). In contrast, the parallel input of potassium chloride caused no significant change in soil reaction, and was not harmful to plant growth.

One reason for the inclusion of potassium fluoride in the present study was the possibility that it may reach the soil as a result of being engendered on or in forage, red clover in particular, through reaction between the hydrofluoric acid from the atmosphere and the chloride of the vegetation. In a related Tennessee station experiment, incorporation of calcium fluoride, alone and with limestone, caused no "observable detrimental effect upon germination or upon sequential seedlings; did not

Table II. Properties of Hartsells Sandy Loam and Clarksville Silt Loam

(Fluorides of potassium and calcium introduced)

Determinations[a]	*Meq. per 100 G. of Dry Soil* *Hartsells sandy loam*	*Meq. per 100 G. of Dry Soil* *Clarksville silt loam*
Exchangeable cations		
Calcium	1.20	1.74
Magnesium	0.40	0.26
Potassium	0.19	0.08
Hydrogen	11.10	4.60
Exchange capacity at pH 7	12.89	6.68
Organic matter, %	5.00	3.60
pH values in water	5.40	5.60

[a] Exchangeable Ca and Mg determined by neutral normal ammonium acetate extraction and leaching of 10 g. of soil with 250 ml. of solution; exchangeable H determined by replacement with 250 ml. 0.5*M* neutral Ca acetate and titration of engendered acidity with 0.1*N* $Ba(OH)_2$ to pH 8.8 (*15*). Exchange capacity is expressed as summation of Ca, Mg, K, and H. Determination of "organic matter" by means method of Walkley and Black (*16*).

Table I. Analyses of Soils Used for Inputs of Potassium and Calcium Fluorides[a]

Soil	*Fluorine, P.P.M.*	K_2O, %	Ca[b], %	Mg[b], %	Mn, %	Fe_2O_3, %	Al_2O_3, %	P_2O_5, %
Hartsells fine sandy loam	169	0.139	0.20	0.58	0.11	4.03	2.93	0.035
Clarksville silt loam	160	0.066	0.32	0.12	0.09	3.23	0.65	0.035

[a] $HCl-HNO_3$ digestion.
[b] Expressed as $CaCO_3$ equivalence.

Table III. Six-Year Leachings and Retentions of Fluorine from Incorporations of Potassium and Calcium Fluorides and from Quenched Electric Furnace Slag

(Limestoned and wollastonited)

Incorporations per 2,000,000 Lb. of Scil				Annual Leachings of Fluorine, Lb./per 2,000,000 Lb. Soil									
Fluorides[a]		Liming Additions		Fluorine							Increase[c]	Fluorine Retention[d]	
KF	CaF_2	Type	Rate[b]	1st	2nd	3rd	4th	5th	6th	Total	Lb.	Lb.	%
				IN HARTSELLS SOIL									
None		None		0.52	0.67	0.60	0.51	0.98	0.78	4.06[e]	...	...	..
		L.S.	Light	1.81	0.86	0.78	0.97	1.08	0.98	6.48	2.42	...	..
		L.S.	Heavy	2.05	1.14	0.65	0.78	1.16	0.84	6.62	2.56	...	..
		Woll.	Light	1.71	0.82	1.03	0.62	0.93	0.72	5.83	1.77	...	..
		Woll.	Heavy	7.89	7.65	1.14	0.75	0.84	0.92	19.19	15.13	...	..
		Slag[f]	Coarse[g]	1.38	1.50	2.99	6.37	7.62	7.77	27.63	23.57	376	94
		Slag[f]	100-mesh	3.67	5.29	7.77	11.18	7.51	7.83	43.25	39.19	361	90
KF	...	None	None	6.62	1.61	7.20	6.01	9.22	7.83	38.49	34.43	366	92
KF	...	L.S.	Light	2.14	2.40	3.23	4.78	3.29	2.63	18.47	16.05	384	96
KF	...	L.S.	Heavy	4.87	4.03	6.54	7.35	8.02	5.39	36.20	33.64	366	92
KF	...	Woll.	Light	2.06	1.58	3.30	3.40	3.53	2.53	16.40	14.63	385	96
KF	...	Woll.	Heavy	10.36	9.27	7.40	9.31	9.42	7.26	53.02	37.89	362	91
...	CaF_2	None		6.63	2.77	11.10	8.33	9.90	6.09	44.82	40.76	359	90
...	CaF_2	L.S.	Heavy	4.48	3.51	4.52	5.19	5.34	3.83	26.87	24.31	376	94
...	CaF_2	Woll.	Heavy	9.38	6.90	4.86	4.87	5.08	3.65	34.74	19.61	380	95
				IN CLARKSVILLE SOIL									
None		None		0.93	0.44	1.16	0.95	1.31	1.35	6.14[e]	...	...	..
		L.S.	Light	0.65	0.42	0.70	0.94	1.41	0.93	5.05	−1.09	...	..
		L.S.	Heavy	0.96	0.72	0.98	0.88	1.42	1.09	6.05	−0.09	...	..
		Woll.	Light	1.05	0.43	0.58	0.77	1.56	0.75	5.14	−1.00	...	..
		Woll.	Heavy	8.08	7.08	2.32	0.92	1.20	1.13	20.73	14.59	...	..
		Slag[f]	Coarse[g]	3.70	5.96	15.41	18.98	19.21	21.87	85.13	78.99	321	80
		Slag[f]	100-mesh	11.43	8.85	47.93	26.72	25.47	23.17	143.57	137.43	263	66
KF	...	None	None	4.80	2.80	6.95	9.68	7.99	7.40	39.62	33.48	367	92
KF	...	L.S.	Light	6.33	4.92	8.30	7.21	5.07	4.97	36.80	37.89	362	91
KF	...	L.S.	Heavy	10.20	7.53	15.96	12.08	9.44	11.68	66.89	66.98	333	83
KF	...	Woll.	Light	7.08	3.20	8.52	8.55	5.72	6.00	39.07	40.07	360	90
KF	...	Woll.	Heavy	20.62	15.59	16.55	13.04	14.51	12.00	92.31	77.72	322	81
...	CaF_2	None		5.38	2.73	16.65	11.26	8.98	8.23	53.23	47.09	353	88
...	CaF_2	L.S.	Heavy	5.55	4.68	5.24	4.93	4.86	4.49	29.75	29.84	370	93
...	CaF_2	Woll.	Heavy	8.93	6.38	3.92	3.72	4.03	3.99	30.97	16.38	384	96
Rainfall, inches per annum				61.06	58.50	45.67	47.11	48.79	37.63	298.76			

[a] Each fluoride incorporation supplied fluorine at 200-lb. rate at beginnings of 1st and 3rd years.

[b] 100-mesh incorporations of limestone and fused wollastonite furnished calcium in equivalence to 6000 lb. of $CaCO_3$ for light rate and 18,000 lb. for heavy rate in Hartsells soil; 4000 and 12,000 lb. for Clarksville soil.

[c] Above outgo from untreated soil.

[d] From 400-lb. input, after applications of respective values for "increase" in no-addition controls.

[e] Six and 0.35 lb. less than amount brought down by rain waters for Hartsells soil, 4 and 0.27 lb. for Clarksville soil.

[f] Fluorine input of 400 lb. of fluorine (as slag) per acre required first- and third-year incorporation of 8888 lb. of slag, of 2.25% fluorine content.

[g] From 400-lb. inputs.

promote plant growth; was not adequate as a source of nutrient calcium; and was of nugatory value as a liming material" (*9*).

In the experiments by Hurd-Karrer (*3*) and in two experiments at the New Jersey station (*4*, *13*), the injurious effects of additive hydrofluoric acid upon plant growth were eliminated by soil liming and the engendered calcium fluoride caused no increase in fluorine uptake.

Objectives

As an alternative explanation of their findings that phosphatic fertilizers had caused no increase in the fluorine content of forage collected by them, Hart, Phillips, and Bohstedt (*2*) suggested that the calcium fluoride inclusions had passed into ground waters. That postulation could not be verified then because of the lack of a lysimeter study of the behavior of calcium fluoride in the soil. Although incorporations of sodium and magnesium fluorides, sodium silicofluoride, cryolite, and rock phosphate were compared by means of leaching outgo and plant uptake of fluorine in an extensive lysimeter study (*11*), incorporations of the fluorides of potassium and calcium had not been included. Hence, those two fluorides were compared during the 6 years of the present experiment, the objectives of which were to distinguish between recoveries of fluorine from equivalent incorporations of the two fluorides, with and without liming materials; to ascertain the fate of the potassium of the fluoride and of the slag; and to integrate the potential exchange reactions and repressions that would govern the proportions of the dominant cations carried by the rainwater drainage. A corollary objective was to establish the tendencies of limestone and fused wollastonite to induce differences in the leachings of fluorine from the materials native to the soils and from the two additive fluorides (*6*).

Experimental

Compositions and properties of the Hartsells sandy loam and the Clarksville silt loam used are indicated in Tables I and II. A pertinent distinction is the fact that the alumina content of the Hartsells soil was 4.5 times the alumina content of the Clarksville soil. Each placement of soil was from a screened moist bulk and represented 100 pounds on a moisture-free basis, in an outdoor lysimeter of $^1/_{20,000}$-acre area. The soils were maintained clean and fallow throughout the 6 years of the experiment.

The initial incorporations of two fluorides, and of the slag, supplied 200 pounds of fluorine per acre and were repeated at the beginning of the third year. The control incorporations of the three liming materials are detailed for the two soils in Table III. The soils were wetted only by rainfall and the drainage waters were collected periodically. Fluorine was determined in every collection by means of the procedure developed by the American Public Health Association (*1*); and, wherever necessary, the leachings were clarified and decolorized through use of the procedure evolved by Shaw (*14*).

Fluorine Recoveries

Rain waters brought 10.41 pounds of fluorine in the 6 years of the experiment and that increment was regarded as a natural content of fluorine in the severally treated soils. Because of the relatively small quantities of fluorine in the leachings within the first 2 years, from the Hartsells soil in particular, the 200-pound inputs of the initial year were repeated at the beginning of the third year and effects were registered by the recoveries of fluorine in that year (Table III).

The light-rate control incorporations of limestone and wollastonite caused slight increases in the total outgo of fluorine from the supplies native to the Hartsells soil but not from the Clarksville controls. However, no total fluorine outgo from those six calcium-fortified controls was equal to the amount of fluorine the rain waters brought to the fallow soils in 6 years.

In contrast, the heavy-rate incorporations of wollastonite caused appreciable increases in the outgo of fluorine from the supplies native to both soils, especially in the initial 3 years of the experiment. Earlier findings indicated that upon decomposition of calcium silicate in the soil, the liberated solvated silica causes increases in the outgo of calcium and fluorine (*8*). Apparently, the silica released from the larger inputs of wollastonite served to offset the "common-ion effect" exerted by the calcium of the other three liming controls upon the leachings of calcium fluoride from each soil.

The several annual passages of fluorine from the 100-mesh slag in the two soils were virtually twice the corresponding passages from the coarse slag, and the leachings of fluorine from the slagged Clarksville soil of higher natural content of exchangeable calcium were 3.5 times the corresponding leachings from the decidedly more acidic Hartsells soil. The recoveries from the coarse and 100-mesh slag were 5.9 and 9.8% for Hartsells and 19.8 and 34.4% for Clarksville (Table III). These differences may reflect the larger proportion of calcium exchange for the hydrogen of the more acidic Hartsells soil and, consequently, less residues of the more soluble silicofluoride of the incorporated slag.

The recoveries from the 400-pound (2 × 200) inputs of fluorine as potassium fluoride in the Hartsells soil were repressed by the light incorporations of

Table IV. Six-Year Outgo of Potassium Induced by Incorporations of Potassium and Calcium Fluorides, and as Quenched Electric Furnace Slag

(Limestoned and wollastonited)

Incorporation per 2,000,000 Lb. of Soil				*Annual Leachings of Potassium, Lb. K_2O per 2,000,000 Lb. Soil*									
Fluorides[a]		*Liming Additions*		*Potassium*							*Increase*[c]	*Potassium Recovery*[d]	
KF	*CaF_2*	*Type*	*Rate*[b]	*1st*	*2nd*	*3rd*	*4th*	*5th*	*6th*	*Total*	*Lb.*	*Lb.*	*%*
IN HARTSELLS SOIL													
None		None		87.6	45.0	20.1	15.7	17.0	13.0	198	...	...	..
		L.S.	Light	26.0	18.4	15.9	15.3	13.5	10.7	100	−98	...	..
		L.S.	Heavy	23.8	19.2	16.1	11.4	9.1	6.2	86	−112	...	..
		Woll.	Light	29.4	17.0	15.5	13.0	12.2	9.6	97	−101	...	..
		Woll.	Heavy	17.7	10.3	12.2	7.3	3.8	3.6	55	−143	...	..
		Slag[e]	Coarse	43.3	11.9	9.4	10.8	10.6	6.5	93	−105	0	0
		Slag[e]	100-mesh	26.0	14.8	11.4	13.0	9.9	6.2	81	−117	0	0
KF	...	None	None	280.9	136.8	65.8	109.8	88.4	49.5	732	534	534	54
KF	...	L.S.	Light	141.5	78.6	115.0	97.4	79.2	46.1	558	360	458	46
KF	...	L.S.	Heavy	160.7	90.7	107.4	94.2	62.2	37.3	552	354	466	47
KF	...	Woll.	Light	131.5	66.2	101.8	81.3	75.5	42.5	499	301	402	41
KF	...	Woll.	Heavy	110.2	56.9	67.9	78.9	54.8	31.8	401	203	346	35
...	CaF_2	None		67.6	39.5	16.2	11.9	16.0	10.0	161	−37	0	..
...	CaF_2	L.S.	Heavy	23.4	19.3	11.5	10.7	8.4	6.4	79	−119	0	..
...	CaF_2	Woll.	Heavy	16.5	11.2	7.3	7.9	6.6	5.0	55	−143	0	..
IN CLARKSVILLE SOIL													
None		None		45.6	23.7	16.0	11.5	13.0	10.9	121	...	...	..
		L.S.	Light	24.4	21.5	12.4	11.2	10.9	9.0	89	−32	...	..
		L.S.	Heavy	32.9	19.8	14.9	10.1	10.2	5.8	94	−27	...	..
		Woll.	Light	19.0	15.2	33.2	11.1	12.0	6.9	98	−23	...	..
		Woll.	Heavy	26.2	11.8	12.1	7.8	8.8	5.6	73	−48	...	..
		Slag[e]	Coarse	35.7	19.2	16.3	13.7	14.9	10.4	110	−11	...	..
		Slag[e]	100-mesh	40.6	16.0	21.7	12.5	14.3	8.5	114	−7	...	..
KF	...	None	None	258.3	91.4	163.7	103.7	78.5	48.8	745	624	624	63
KF	...	L.S.	Light	292.4	78.0	192.7	89.6	58.2	41.7	753	632	664	67
KF	...	L.S.	Heavy	314.8	73.6	186.4	76.0	55.6	39.1	745	624	651	66
KF	...	Woll.	Light	230.7	65.5	191.1	95.2	65.6	47.5	696	575	598	60
KF	...	Woll.	Heavy	231.9	74.4	122.9	82.6	71.0	39.0	622	501	549	55
...	CaF_2	None		43.2	21.7	16.2	9.1	11.7	10.3	112	−9	...	..
...	CaF_2	L.S.	Heavy	36.7	17.6	12.5	7.8	11.2	7.8	94	−27	...	..
...	CaF_2	Woll.	Heavy	23.8	12.1	8.0	6.6	9.1	7.8	68	−44	...	..
Rainfall, inches per annum				61.06	58.50	45.67	47.11	48.79	37.63	298.76			

[a] Incorporations of KF at beginning of first and third years provided 991-lb. total inputs of K_2O.

[b] 100-mesh incorporations of limestone and fused wollastonite furnished calcium in equivalence to 6000 lb. of $CaCO_3$ for light rate and 18,000 lb. for heavy rate in Hartsells soil; 4000 and 12,000 lb. in Clarksville soil.

[c] Above outgo from untreated soil.

[d] From the input of 991-lb. K_2O equivalence of 400-lb. input of fluorine, with relationships to five controls that received no KF.

[e] Fluoric components of slag supplied 400-lb. inputs of fluorine.

Table V. Six-Year Outgo of Calcium and Magnesium Induced by Incorporations of Potassium and Calcium Fluorides and by Quenched Electric Furnace Slag

(Limestoned and wollastonited)

Incorporations				*Annual Leachings, Lb. per 2,000,000 Lb. Soil*													
Fluorides		*Liming Additions*		*Calcium as $CaCO_3$ Equiv.*							*Magnesium as $CaCO_3$ Equiv.*						
KF	*CaF_2*	*Type*	*Rate*[a]	*1st*	*2nd*	*3rd*	*4th*	*5th*	*6th*	*Total*	*1st*	*2nd*	*3rd*	*4th*	*5th*	*6th*	*Total*
IN HARTSELLS SOIL																	
None		None		426	138	156	154	162	128	1164	136	43	39	44	45	26	333
		L.S.	Light	1131	389	378	367	291	249	2805	51	24	26	47	26	16	190
		L.S.	Heavy	2511	1124	1024	807	539	430	6435	16	8	9	14	8	2	57
		Woll.	Light	1070	423	373	361	252	248	2727	62	26	31	28	23	15	185
		Woll.	Heavy	2924	1037	827	606	319	382	6095	36	21	22	25	14	7	125
		Slag[b]	Coarse	795	419	789	942	525	389	3859	86	24	38	33	16	3	200
		Slag[b]	100-mesh	1271	403	1452	858	464	378	4826	66	25	45	28	17	6	187
KF	. . .	None	None	293	72	98	108	134	96	801	95	24	28	29	41	21	238
KF	. . .	L.S.	Light	999	378	355	313	304	198	2547	48	20	37	28	28	15	176
KF	. . .	L.S.	Heavy	2585	1241	888	776	545	397	6432	17	12	11	13	8	1	62
KF	. . .	Woll.	Light	1016	314	314	303	255	174	2376	64	21	29	25	23	7	169
KF	. . .	Woll.	Heavy	2943	1025	787	677	422	304	6158	41	15	26	23	15	4	124
. . .	CaF_2	None		501	163	225	192	219	116	1416	104	35	33	31	34	15	252
. . .	CaF_2	L.S.	Heavy	2106	1213	995	753	565	355	5987	14	6	10	10	9	2	51
. . .	CaF_2	Woll.	Heavy	3054	1152	759	656	399	370	6390	38	19	20	22	16	11	126
IN CLARKSVILLE SOIL																	
None		None		325	275	277	201	240	161	1479	134	87	87	62	67	33	470
		L.S.	Light	964	554	435	373	302	256	2884	118	77	58	55	45	31	384
		L.S.	Heavy	1553	1151	863	704	605	372	5248	77	45	33	31	27	11	224
		Woll.	Light	826	491	496	326	320	157	2616	116	65	68	51	50	20	370
		Woll.	Heavy	2630	1080	668	633	497	291	5799	75	40	37	36	33	15	236
		Slag[b]	Coarse	973	846	1003	985	791	603	5201	154	62	54	30	23	11	334
		Slag[b]	100-mesh	1688	815	1498	1131	792	578	6502	127	57	48	29	23	16	300
KF	. . .	None	None	240	201	126	166	175	132	1040	108	75	59	61	55	31	389
KF	. . .	L.S.	Light	887	462	332	339	310	236	2566	120	67	55	51	47	31	371
KF	. . .	L.S.	Heavy	1773	1016	682	659	563	423	5116	93	48	35	27	31	17	251
KF	. . .	Woll.	Light	768	320	364	373	327	443	2595	117	54	65	59	53	27	375
KF	. . .	Woll.	Heavy	2635	1086	624	555	434	318	5652	80	46	35	31	32	18	242
. . .	CaF_2	None		388	239	336	270	262	174	1669	135	73	78	59	48	31	424
. . .	CaF_2	L.S.	Heavy	1883	994	843	662	565	402	5349	96	43	35	29	28	14	245
. . .	CaF_2	Woll.	Heavy	2663	1199	701	665	575	373	6176	75	47	34	42	37	23	258
Rainfall, inches per annum				61.06	58.50	45.67	47.11	48.79	37.63	298.76							

[a] 100-mesh incorporations of limestone and fused wollastonite furnished calcium in equivalence to 4000 lb. of $CaCO_3$ for light rate and 12,000 lb. for heavy rate, per 2,000,000 lb. of soil in Clarksville soil; 6000 and 18,000 lb. in Hartsells soil.

[b] Input of 400 lb. of fluorine per acre required first- and third-year incorporations of 8888 lb. of slag that contained 2.25% of fluorine.

limestone and wollastonite, but not by the heavy-rate incorporations. The recovery from the calcium fluoride alone was greater than the recovery from potassium fluoride alone, but the outgo of fluorine from the calcium fluoride (Table III) was repressed substantially by both liming materials.

At light rate the liming materials did not diminish the recoveries from the potassium fluoride in the Clarksville soil, whereas at heavy rate both liming materials caused decided increases in the recoveries from potassium fluoride. This variation was registered in the six annual collections from both limestone and wollastonite (Table III). Likewise, recovery from calcium fluoride in the unlimed Clarksville soil exceeded the recovery from the potassium fluoride parallel and recoveries from the calcium fluoride were diminished greatly by both liming materials. Obviously, the concentration of engendered solutes of calcium was such that the common-ion effect overcame the tendency of the wollastonite-derived solvated silica to increase migration of calcium and fluorine into the soil drainage (*8*). Thus in unlimed and lightly limed Hartsells and Clarksville soils the plant uptake of fluorine from added calcium fluoride might exceed the uptake of fluorine from equivalent incorporations of potassium fluoride. But the heavy liming of those two soils would lessen the capacities of their alumina contents to develop aluminum silicofluoride from the added potassium fluoride, and the plant uptake of fluorine then might exceed the uptake of fluorine from corresponding additions of calcium fluoride. The meager solubility of calcium fluoride would admit only a limited concentration of fluoride ions and the concomitant calcium solutes would be protective against the formation of aluminum silicofluoride through reaction between the alumina of the soil complex and the dissolved calcium fluoride.

Potassium Recoveries

In all 12 comparisons in Table IV the carbonate and silicate minerals lessened the annual leachings of potassium from the supplies native to the two soils. Moreover, in all 28 cases the additions of calcium—as carbonate, wollastonite, slag, or fluoride—caused decreases in potassium recoveries.

Obviously, the values for "increases" and "recoveries" in Table IV are not identical. In all eight limed controls of the upper group in each table, the "increase" was minus and there was no recovery. The values for increases and recovery for the added fluorides in each unlimed soil were identical, because both values connoted the differences between input and outgo. But, in each case of the four combinations of potassium fluoride and a liming material, it was necessary to raise the apparent increase through addition of the specific minus value that resulted from the repression the liming material exerted upon potassium outgo. It is reported in Table V that the additions of potassium fluoride caused decided decreases in the leachings of calcium and magnesium from the two soils, otherwise untreated.

The 400-pound input of fluorine as potassium fluoride supplied 991 pounds

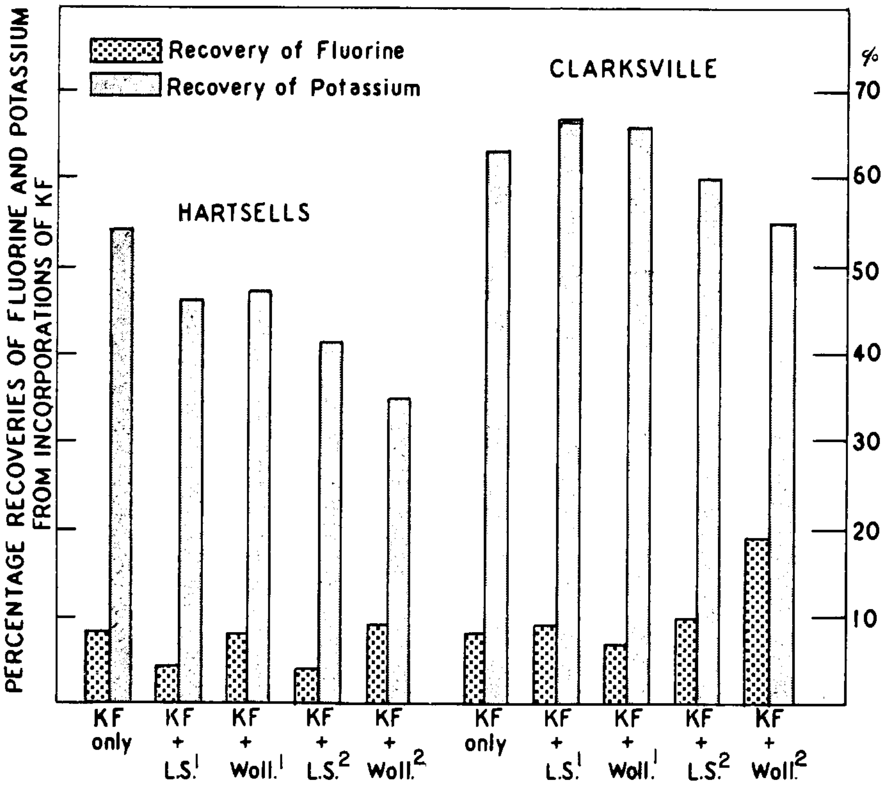

Figure 1. Recovery of fluorine and potassium in 6-year leachings from two 200-pound incorporations of fluorine as potassium fluoride in two soils

With and without limestone and wollastnite at two rates. Fluorine input supplied 991-pound equivalence of K_2O per 2,000,000 pounds of soil

1. Limestone or wollastonite at light rate
2. Limestone or wollastonite at heavy rate

of K_2O per 2,000,000 pounds of soil. After 6 years, the mean of the recoveries from the five cases of that input in the Hartsells soil was 44.6%; against 55.4% mean of retentions of potassium was the corresponding mean of 93.4% for retention of the associated fluorine. The mean for potassium recoveries from the Clarksville soil was 62%, and the companion mean for retentions was 38% (Table IV), compared with the mean of 87.4% for retentions of the associated fluorine. The disparities between the recoveries of fluorine and potassium are depicted for both soils in Figure 1.

The differences between the molal ratios of outgo and corollary retentions of the cation and anion components of the incorporated potassium fluoride register a selective fixation of the fluorine, presumably through precipitation of aluminum fluoride. That result had been indicated by earlier pot culture comparison of potassium fluoride and potassium chloride (*10*), and the fluorine-alumina retention is deemed more probable than a possible smaller fixation of fluorine through fluoride reaction with tricalcium phosphate and resultant formation of apatite (*5*).

Induced Passage of Calcium and Magnesium into Drainage

Limestone, wollastonite, and slag caused increases in outgo of calcium from both soils, including a common increment from rain waters, and in every comparison the heavy-rate liming caused a larger outgo (Table V). In all cases, calcium leachings from the untreated controls, and from the limestoned and wollastonited controls, were largest in the initial year of the experiment, and, in general, were in descending order thereafter (Table V). Exceptions to that order were the relatively heavy third annual passages of calcium from the slag incorporations in both soils.

The potassium fluoride incorporations caused substantial diminutions in the outgo of calcium from both unlimed soils and those that received limestone at light rate (Table V). The largest repression upon calcium outgo was exerted by potassium fluoride alone, and the repressions attributable to the fluoride were lessened appreciably by the carbonate and silica supplements. The 6-year yield of calcium from the heavy input of wollastonite alone was only 63 pounds of calcium carbonate per acre less than the yield from that input plus potassium fluoride in Hartsells and only 147 pounds in Clarksville. Nevertheless, recovery of potassium from the combination of potassium fluoride and heavy-rate input of wollastonite was smallest of the five percentagewise recoveries from each soil, as in the recoveries registered in Table IV.

Calcium fluoride incorporations, alone and with wollastonite, caused significant increases in the leachings of calcium from both soils, and the leachings from the combination of calcium fluoride and wollastonite exceeded those from the wollastonite alone, in both soils; but the results from the combination of fluoride and limestone were less decisive.

Where potassium fluoride additions induce an exchange in the limed soils, as in the simplified equation, $2KF + CaCO_3 \rightarrow CaF_2 + K_2CO_3$, the transition of the fluorine to the less soluble fluoride might be expected to cause a decrease in the outgo of calcium, but such tendency was offset by the dissolving of the calcium from the supplements of carbonate and silicate.

Magnesium leachings from both soils were lessened by limestone and by wollastonite (Table V), alone and in combination with either potassium fluoride or calcium fluoride. The induced decreases in the outgo of magnesium were significant in relation to the inputs of the liming materials and to the quantities of calcium that occurred in the annual collections. In all of the 28 cases in which the several forms of calcium were incorporated, the outgo of magnesium was diminished; however, the largest repressions were exerted by the heavy-rate inputs of limestone, and, in general, were more repressive than the wollastonite inputs. Even though its solubility is of low order, calcium fluoride was uniformly repressive upon magnesium outgo.

In the 30 findings for annual outgo from the two soils, the maximal passage of magnesium occurred in the initial year, and apparently before substantial development of the repressions that were exerted fully by the four calcic materials in all of the 150 collections of annual leachings in the subsequent 5 years.

The lysimeter findings demonstrate that, although the singly incorporated fluorides of potassium and calcium may have induced exchange reactions and attendant reserves of their respective opposites, the two fluorides did not increase the occurrence of magnesium in the free water of the Hartsells and Clarksville soils and this would foretell a lessened plant uptake of magnesium.

Summary

Differential behavior of incorporated fluorides of potassium and calcium was determined, with and without liming materials, in a 6-year lysimeter experiment.

In six of the eight controls, fluorine leachings from the native supplies in Hartsells sandy loam and Clarksville silt loam were less than the increment from rain waters, but the heavy-rate inputs of wollastonite caused significant

increases in outgo of fluorine from both untreated soils.

Fluorine recoveries from the first- and third-year inputs of 200 pounds per acre, as fluorides, were decreased by the liming materials in the Hartsells soil and increased in the Clarksville soil.

Fluorine retentions from potassium fluoride in Hartsells were 91 to 96% against 91 to 92% for Clarksville; minimal retention was from the wollastonite, at heavy rate. The high percentage retentions of fluorine were in contrast to the potassium retentions of 46 to 65% by Hartsells and 33 to 45% by Clarksville. Such differentials demonstrate the preferential fixation of the fluoride ion, the extent being higher in the soil of lower content of calcium and higher content of alumina (Table I).

Potassium recoveries per annum were greatest after the first- and third-year incorporations. The 28 comparisons demonstrated that all carriers of calcium caused decreases in recoveries of the potassium of the added fluoride.

Potassium fluoride incorporations caused decreases in calcium and magnesium outgo from both soils, whereas calcium fluoride caused enhancements in the leachings of calcium and decreases in outgo of magnesium and potassium from both soils.

In general, wollastonite proved more conducive than limestone in causing fluorine outgo, and was less repressive upon potassium recovery and upon magnesium outgo.

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Received for review September 17, 1954. Accepted June 13, 1955. Presented before the Division of Fertilizer and Soil Chemistry at the 124th Meeting of the AMERICAN CHEMICAL SOCIETY, *New York, N. Y.*

FLUORIDES IN SOIL

Fate and Effects of Hydrofluoric Acid Added to Four Tennessee Soils in a 4-Year Lysimeter Study

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Hydrofluoric acid emissions from thermal processing of rock phosphate have caused abnormal occurrences of fluorine in the atmosphere and vegetation in Maury County, Tennessee. Because of the uncertainty as to the effects of atmosphere-derived hydrofluoric acid upon soils, a dilute solution of that acid was used for applications and incorporations to four Tennessee soils in a 4-year lysimeter experiment, through which rainwater leachings of fluorine, calcium, magnesium, and potassium were determined. Fluorine leachings from the incorporations greatly exceeded those from the applications. Retentions of fluorine from the 200- and 800-pound additions ranged between 75.8 and 99.6% of the inputs. The fluorine retentions by the four soils were proportional to their contents of aluminum, and were postulated as due to the formation of aluminum silicofluoride, $Al_2(SiF_6)_3$. The hydrofluoric acid additions caused small decreases uniformly in the leachings of calcium and magnesium. When integrated with plant responses obtained in earlier pot culture experiments, the findings indicate that the fertility of a soil will not be impaired by hydrofluoric acid that may come to it from the atmosphere.

HYDROFLUORIC EMISSIONS occur in the thermal production of ortho- and metaphosphate fertilizers and in the preparatory nodulization of rock phosphate charges for reduction in electric furnaces (*9*). The emitted acid undergoes dispersion in the gaseous phase, as mists and as droplets, according to height of release, topography, atmospheric moisture, and meteorological conditions. Emissions of hydrofluoric acid in the manufacture of aluminum also have been blamed for abnormal fluorine contents of vegetation in several states (*1, 2, 6*) and as a result of studies conducted at the experiment stations of Oregon (*5*), Washington (*5, 17*), and Tennessee (*12, 13*).

In bench experiments, Hurd-Karrer (*10*) incorporated "greatly diluted" hydrofluoric acid into a New Jersey soil, the fluorine content of which was only 11 p.p.m. She sought "to determine the extent to which fluorine can be absorbed from soils by plant roots, and the extent to which absorption can be controlled by liming." The effects of addi-