PHOSPHATE FURNACE SLAG vs. LIMESTONE

A 10-Year Lysimeter Study of Soil Liming

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A study was made of the behavior and effect of a phosphate furnace slag after incorporation in the soil and as a possible hazardous source of fluorides in adjacent ground waters. Incorporated slag underwent transition to calcium carbonate, large quantities of which were accounted for as bicarbonate outgo and as cumulative residues. Calcium outgo from the slag, at different input rates and various fineness, exceeded outgo from corresponding inputs of limestone and caused repressions in outgo of magnesium and potassium. Solute outgo from upper-zone incorporations was less than that from full-depth incorporations. Effect of particle size upon outgo was decidedly less for slag than for limestone. The proportions for outgo of calcium were greater in the initial 5 years. The concentrations of fluorides into drainage were attributable to leachings of calcium silicofluoride. The slag proved decidedly more reactive than the limestone, while releasing relatively large amounts of fluoride, passage of which was impeded during drainage through lower strata. Apparently, use of the phosphate furnace slag will not cause detrimental concentrations of fluorides in nearby ground waters.

CALCIUM SILICATE SLAGS are used in several states for soil liming. They are decidedly different from basic slag, which is classified as a phosphatic fertilizer (*1*), not as a "liming material." Calcium silicate slags of different origin are also distinctive among themselves as to composition, structure, and liming value. Steel industry slags contain appreciable contents of manganese, sulfur (*11*), and magnesium and nugatory percentages of phosphorus and fluorine, whereas electric furnace slags carry appreciable quantities of phosphorus and fluorine. Air-cooled phosphate furnace slags are crystalline and dense, but the quenching of the molten slag results in a pitted glass that does not give an x-ray pattern (*5*). The quenched slag of the experiment reported here was from the electric furnace operations at Wilson Dam and was derived from charges that comprised washed brown rock phosphate, quartz, and coke.

Previous Observations

Composition, characteristics, and effectiveness of the slag as a liming material, and its attendant influence upon plant growth and composition have been reported (*6*, *10*, *12–15*). But where charges of unwashed brown rock phosphate or "matrix" were used in an industrial operation of the electric furnace, the resultant slag proved virtually devoid of liming value and hence enormous quantities of calcium and large amounts of included phosphorus of potential fertilizer value are locked within gigantic piles of relatively inert slag.

After slag is incorporated, its silicate content undergoes hydrolysis into calcium hydroxide, which reacts with the acidoids and carbon dioxide of the soil (*6*). A distinctive property of the slag is that suspensions of it in carbon dioxide–impregnated water impart calcium bicarbonate concentrations far beyond those resultant from similar suspensions of calcium carbonate in any form (*7*, *14*). Moreover, fluorine of the slag proved far more dissoluble than fluorine of either fluorspar or precipitated calcium fluoride in laboratory extractions (*5*), or lysimeter drainage waters (*9*). Because of the ready release of the slag-contained fluorine to aqueous systems, it became important to ascertain whether that release would affect uptake of fluorine by vegetation (*13*) and impart high concentrations of fluorides to ground waters.

Objectives

The lysimeter study was inaugurated to determine the behavior of, and effects induced by, incorporations of an electric

Figure 1. Installation of lysimeters

Rain-water drainages pass into building at right

furnace slag of three particle sizes, at three rates, on two soils. Migrations of calcium and concomitant ions in rain-water drainage from the inputs of slag and limestone controls were used to compare the effects of particle size, to compare single *vs.* repetitive incorporations, to establish ratios between total and bicarbonate leachings, and to differentiate between conservation of calcium from upper-half and full-depth incorporations. The findings for outgo of calcium and other components were to be supplemented by determinations of the residues of carbonates from those engendered. A major consideration was to determine the occurrence of fluorine in the drainage waters from the variously slagged soils, and whether the repetitive incorporations of the slag at rational rates and single heavy-rate inputs would impart a harmful concentration of fluorine to immediate ground waters.

Experimental Work

Slag and Limestone

The quenched slag contained 52.7% calcium oxide, 34.9% silica, 1.25% phosphorus pentoxide, 0.29% sulfide sulfur (*18*), 0.23% of potassium oxide, and 3.20% of fluorine, and had a neutralization value equivalent to an 84% limestone (*17*). The "4-mesh" slag comprised 99% of 10-mesh, 74% of 20-mesh, and 16% of 60-mesh screenings. The 4-mesh, 20-mesh, and 100-mesh separates were incorporated as being equivalent to calcium carbonate inputs of 2 tons: four annuals of 2 tons each; 5 tons: four annuals of 5 tons each; and 20 tons, all in relation to 2,000,000 pounds of soil, moisture-free basis, as in Tables III and IV. A limestone of 98.5% calcium carbonate content was used in corresponding make-up as a control for each input of slag.

Soils and Procedures

The Hartsells fine sandy loam and the Baxter silt loam used were acidic (*19*). Their exchange capacities were similar (Table II), but their physical characteristics were different. Seventeen 100-pound charges of each soil, moisture-free basis, were placed upon quartz beds in asphaltum-coated ingot iron lysimeters of 12-inch depth and 1/20,000-acre area. The rain-water drainages passed directly into asphaltum-coated metal containers in the lysimeter building (Figures 1 and 2).

With the exception noted as to group 6, initial and annual inputs were incorporated full depth. The once-slagged soils of groups 1 and 3 were worked up in parallel with the soils of groups 2 and 4, which received additional incorporations. The soils of group 5 were not disturbed after the single incorporations of 100-mesh separates of slag and limestone. The incorporations of 100-mesh slag in the undisturbed units of group 6 were restricted to the upper half of each soil.

Procedures prescribed by the Association of Official Agricultural Chemists (*1*) were used in the analyses of rain waters and annual composites of the periodic collections of rain-water drainages.

Findings

Rain Waters

Compositions of the ten annual composites of the rain waters caught in the lysimeter "blanks" are reported in Table I. The largest washdown was that of sulfur, as in previous collections that were obtained at several points in Tennessee (*16*). All

Table I. Increments Carried by Rain Waters Collected at Knoxville Lysimeters, 1940–50

	Rain Waters		Components Brought to Soil, Pounds per Acre					
Period	Inches per annum	pH	Ca[a]	Mg[a]	SO_4	K	P	N
1940–41	31.85	...	95	22	133	9	...	...
1941–42	41.06	...	93	25	163	12	...	...
1942–43	57.88	7.4	130	25	143	7	0.1	8
1943–44	51.19	7.1	115	19	123	9	0.2	7
1944–45	55.60	7.1	108	19	153	9	0.1	6
1945–46	53.81	6.9	123	22	173	6	0.1	6
1946–47	50.98	7.7	138	25	163	7	0.1	2
1947–48	42.69	6.7	98	31	234	16	0.3	6
1948–49	56.57	7.0	90	38	158	15	0.8	9
1949–50	62.60	6.7	100	31	95	14	0.6	4
10-year total	504.23		1090	257	1538	104	2.3[b]	48[b]
Average annual	50.4		109	26	154	10	0.3	6

[a] Expressed as $CaCO_3$ equivalence.

[b] Computed from 8 to 10 years.

Table II. Exchangeable Bases[a] and pH for Hartsells Fine Sandy Loam and Baxter Silt Loam Controls before and after 10-Year Rain-Water Leachings

	Hartsells Fine Sandy Loam, Meq.		Baxter Silt Loam, Meq.	
Base	Initially	After 10 years	Initially	After 10 years
Calcium	1.68	0.88	1.48	1.10
Magnesium	0.25	0.15	0.36	0.19
Potassium	0.13	0.09	0.14	0.09
Hydrogen[b]	4.39	3.91	3.97	3.70
Exchange capacity[c]	6.45	5.03	5.95	5.08
pH	5.0	5.2	5.2	5.4
CO_3	0.0	0.0	0.0	0.0

[a] Millequivalents per 100 grams of dry soil.

[b] Difference between sum of Ca, Mg, and K and exchange capacity (*19*).

[c] Obtained by ammonium acetate extraction at pH 7.0.

collections of rain waters of the earlier and present experiments were slightly alkaline, probably because of occurrence of smoke-borne silicates and limestone road dust in the atmosphere. Consideration of the occurrences of calcium, magnesium, potassium, and sulfate in the rain waters is primarily for comparisons with corresponding derivations in the drainage from the untreated soils.

Exchangeable Base Contents The "after 10 years" values of Table II integrate the effect of the leachings from the systems native to the two soils and passages of the increments of cations and ions that the rainwaters brought to the soils. The 10-year rainfall of 504 inches caused both control soils to suffer significant diminutions in their contents of exchangeable calcium, magnesium, potassium, and hydrogen, with resultant decreases in exchange capacity and slight elevations in pH values. The control soils were devoid of determinable carbonate content, initially and finally.

Calcium Outgo

The chemical fate of the calcium of incorporated liming materials is governed

Table III. Calcium Outgo in 10-Year Rain-Water Leachings from Equivalent Incorporations of Limestone and Slag in Hartsells Fine Sandy Loam

	Incorporations[a]				*Annual Outgo, Pounds $CaCO_3$ Equivalence per Acre, 2,000,000 Pounds of Soil*											*Outgo*
Group	*Materials*	*Mesh*	*Tons*	*No.*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*Total*	*Increase*[b]
	None	...	...	.	281	361	220	226	173	135	117	141	159	193	2006	918[c]
1	Limestone	20	2	1	636	808	442	524	300	278	211	258	260	255	3972	1966
	Slag	20	2	1	574	809	450	541	231	310	220	261	289	315	4090	2084
	Limestone	100	2	1	724	853	437	486	376	293	230	253	293	323	4268	2262
	Slag	100	2	1	660	772	450	490	338	289	234	295	291	302	4121	2115
2	Limestone	20	2	4	575	1313	984	1064	801	666	566	512	656	770	7907	5901
	Slag	20	2	4	627	1373	1562	2012	1249	1072	783	727	783	804	10992	8986
	Limestone	100	2	4	721	1501	948	1362	885	829	674	649	771	887	9227	7221
	Slag	100	2	4	668	1565	2052	1977	1307	1045	770	646	701	723	11454	9448
3	Limestone	4	5	1	818	1255	850	930	597	516	414	407	465	541	6793	4787
	Slag	4	5	1	789	1405	945	720	561	522	430	448	506	454	6780	4774
4	Limestone	4	5	4	781	1465	1034	1175	830	790	595	664	762	869	8965	6959
	Slag	4	5	4	833	2312	1876	1992	1346	1452	1229	1146	1346	1527	15059	13053
5	Limestone	100	20[d]	1	1216	1262	930	1024	804	813	710	643	770	922	9094	7088
	Slag	100	20[d]	1	1274	1849	1576	1722	1263	1180	830	766	1079	1173	12712	10706
6	Slag	100	20[d]	1	626	758	744	934	804	964	776	806	1075	1206	8693	6687
	Slag	100	10[d]	1	660	752	626	837	686	743	567	636	827	961	7295	5289
	Rainfall, inches				31.85	41.06	57.88	51.19	55.60	53.81	50.98	42.69	56.57	62.60	504.23	

[a] Basis of $CaCO_3$ equivalence. Full-depth incorporations for groups 1–5; half-depth for group 6.

[b] Net losses in relation to controls.

[c] Net loss from untreated soil, or difference between outgo and increment from rain waters, 918 pounds.

[d] Soil undisturbed during 10 years.

Table IV. Calcium Outgo in 10-Year Rain-Water Leachings from Equivalent Incorporations of Limestone and Slag in Baxter Silt Loam

	Incorporations[a]				*Annual Outgo, Pounds $CaCO_3$ Equivalence per Acre, 2,000,000 Pounds of Soil*											*Outgo*
Group	*Materials*	*Mesh*	*Tons*	*No.*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*Total*	*Increase*[b]
	None	...	...	.	270	305	195	269	208	150	130	137	150	171	1985	897[c]
1	Limestone	20	2	1	590	845	421	516	353	289	247	248	279	299	4087	2102
	Slag	20	2	1	592	821	389	508	336	287	254	268	311	301	4067	2082
	Limestone	100	2	1	678	852	342	508	349	288	237	260	300	292	4106	2121
	Slag	100	2	1	639	709	492	547	361	316	249	273	314	316	4216	2231
2	Limestone	20	2	4	573	1225	738	1128	905	696	611	629	701	816	8002	6017
	Slag	20	2	4	607	1184	1209	1741	1247	994	773	764	830	918	10267	8282
	Limestone	100	2	4	666	1163	1023	1073	1010	733	659	618	712	969	8626	6641
	Slag	100	2	4	618	1722	1643	1755	1243	1071	783	677	678	860	11050	9065
3	Limestone	4	5	1	725	1100	656	913	601	530	446	404	538	651	6564	4579
	Slag	4	5	1	928	1278	871	827	755	518	449	412	547	618	7203	5218
4	Limestone	4	5	4	693	1218	830	1000	862	760	577	670	734	911	8355	6370
	Slag	4	5	4	917	1439	1228	1697	1469	1253	1012	991	1157	1376	12539	10554
5	Limestone	100	20[d]	1	1024	1220	925	909	846	676	581	612	723	879	8415	6430
	Slag	100	20[d]	1	1397	1608	1228	1537	1211	1058	942	753	1001	1299	12034	10049
6	Slag	100	20[d]	1	444	607	618	883	833	823	759	715	894	1187	7763	5778
	Slag	100	10[d]	1	533	392	441	644	653	739	704	614	804	1012	6536	4551
	Rainfall, inches				31.85	41.06	57.88	51.19	55.60	53.81	50.98	42.69	56.57	62.60	504.23	

[a] Basis of $CaCO_3$ equivalence. Full-depth incorporations for groups 1–5; half-depth for group 6.

[b] Net losses in relation to controls.

[c] Net loss from untreated soil, or difference between outgo and increment from rain waters, 897 pounds.

[d] Soil undisturbed during 10 years.

by several factors—exchange for the hydrogen of soil acidoids; outgo as bicarbonate, nitrate, and sulfate; uptake by vegetation; and probable crystallization and geochemical aging of engendered calcium complexes. Obviously, the outgo from a limed soil under fallow will be governed by the nature of the liming material, by its particle size, by rate and depth of incorporations, by seasonal effects, by bacteriological activities, and by the quantity and periodicity of rainfall.

Yearly and 10-year totals and "outgo increases" of calcium from the Hartsells and Baxter soils are given in Tables III and IV. The calcium carbonate–equivalent mean of the annual leachings of calcium from each untreated soil was close to 90 pounds more than the corresponding mean for rain-water increments.

In every case of outgo from single incorporations of full depth—groups 1, 3, and 5 for both soils—the maximal occurred in the second year. Increases in total outgo from the 2-ton incorporations of the 20- and 100-mesh limestone and slag (group 1) were comparable for the two soils and were close to one half of the inputs. Calcium leachings from the repetitive 4 × 2 ton inputs of slag (group 2, four annual 2-ton inputs) were substantially greater than those from the control inputs of limestone. In comparison against the near-constant outgo from 2-ton inputs of the two liming materials, the increases in calcium outgo from the four successive incorporations of 2 tons per annum in group 2 were three to one for the limestone and four to one for the slag in both soils.

Increases in calcium outgo from the 5-ton incorporations of 4-mesh slag and limestone in the two soils (group 3, Tables III and IV) were close to equivalences of 2.5 tons of calcium carbonate. The four 5-ton-per-annum inputs of the 4-mesh limestone (group 4) caused 10-year outgo increases of more than 3 tons of calcium carbonate per acre from both soils, but the mean of those increases was only 47% of the mean of the increases from the slag.

Maximal increase in outgo of calcium came from the four 5-ton annual incorporations of the 4-mesh slag in both soils, and in every case outgo from both 4-mesh materials was largest in the second year, group 4. The next largest totals were those from the 20-ton incorporations of 100-mesh slag in the undisturbed soils (group 5, Tables III and IV). In the first year the largest outgo from the six groups of both soils was from the 20-ton incorporations of slag in those groups, and in subsequent years the losses of calcium from the slagged soils of those groups were far greater than the losses from the corresponding limestoned soils.

The 20-ton full-depth incorporations of 100-mesh materials in groups 5 and 6 of Tables III and IV were not disturbed throughout the 10 years of the lysimeter experiment. After the initial year, leachings of calcium from the 20-ton input of slag exceeded the outgo from the related 10-ton inputs, but the increases in outgo were not proportionate to input. The substantial difference between the leachings of calcium from full-depth and half-depth incorporation may be accounted for in part by a greater degree of carbonate conversion of the silicate to carbonate in the full depth of soil and by some retention of the calcium solutes during their passage through the lower unslagged zone.

By 5-Year Periods. Frequently, it is necessary to consider the proper interval between an initial liming and a second one. Recorded for both soils in Table V are total and net passages as pounds of calcium carbonate equivalence per acre and as percentage of input for the initial and second 5 years, as results of rainfall means of 48 and 53 inches. The passages of calcium from the single 2-ton incorporations in both soils were in the range of 35 to 40% of input in the first 5 years and about 16% in the second 5 years. Passages from the four annual 2-ton incorporations of both liming materials exceeded greatly the corresponding losses from the single 2-ton incorporations in the first 5 years, but percentage losses from the slag were somewhat similar for the two periods. In both 5-year intervals the largest increases in outgo of calcium were those from the 20-ton incorporations of slag in groups 4, 5, and 6 of both soils.

In most cases net outgo of calcium from a full-depth input of a liming material was smaller in the second 5 years, as in groups 1 to 5 for both soils. The reverse was true for half-depth incorporations of both liming materials in both

Table V. Calcium Outgo in First and Second 5 Years from Equivalent Incorporations of Limestone and Slag in Two Soils

					Outgo, Pounds $CaCO_3$ Equivalence per 2,000,000 Pounds of Soil											
					From Hartsells Fine Sandy Loam						From Baxter Silt Loam					
					First 5 Years			Second 5 Years			First 5 Years			Second 5 Years		
	Incorporations[a]					Net			Net			Net			Net	
Group	Materials	Mesh	Tons	No.	Total lb.	Lb.	% of input	Total lb.	Lb.	% of input	Total lb.	Lb.	% of input	Total lb.	Lb.	% of input
	None	...	...	.	1261	...	..	745	...	..	1247	...	..	738	...	..
1	Limestone	20	2	1	2710	1449	36	1262	517	13	2725	1478	37	1362	624	16
	Slag	20	2	1	2695	1434	36	1395	650	16	2646	1399	35	1421	683	17
	Limestone	100	2	1	2876	1615	40	1392	647	16	2729	1482	37	1377	639	16
	Slag	100	2	1	2710	1449	36	1411	666	17	2748	1501	38	1468	730	18
2	Limestone	20	2	4	4737	3476	22	3170	2425	15	4569	3322	21	3433	2695	17
	Slag	20	2	4	6823	5562	35	4169	3424	21	5988	4741	30	4279	3541	22
	Limestone	100	2	4	5417	4156	26	3810	3065	19	4935	3688	23	3691	2953	18
	Slag	100	2	4	7569	6308	39	3885	3140	20	6981	5734	36	4069	3331	21
3	Limestone	4	5	1	4450	3189	32	2343	1598	16	3995	2748	27	2569	1831	18
	Slag	4	5	1	4420	3159	32	2360	1615	16	4659	3412	34	2634	1896	19
4	Limestone	4	5	4	5285	4024	10	3680	2935	15	4703	3456	9	3652	2914	7
	Slag	4	5	4	8359	7098	18	6700	5955	29	6750	5503	14	5789	5051	13
5	Limestone	100	20[b]	1	5236	3975	10	3858	3113	8	4924	3677	9	3491	2753	7
	Slag	100	20[b]	1	7684	6423	16	5038	4293	11	6981	5732	14	5053	4315	11
6	Slag	100	20[b]	1	3866	2605	7	4827	4082	10	3385	2138	5	4378	3640	9
	Slag	100	10[b]	1	3561	2300	12	3734	2989	15	2663	1416	7	3873	3135	16
	Rainfall, inches				241.67			266.65			241.67			266.65		

[a] In $CaCO_3$ equivalence. Full-depth incorporations for groups 1–5; half-depth for group 6.

[b] Soil undisturbed during 10 years.

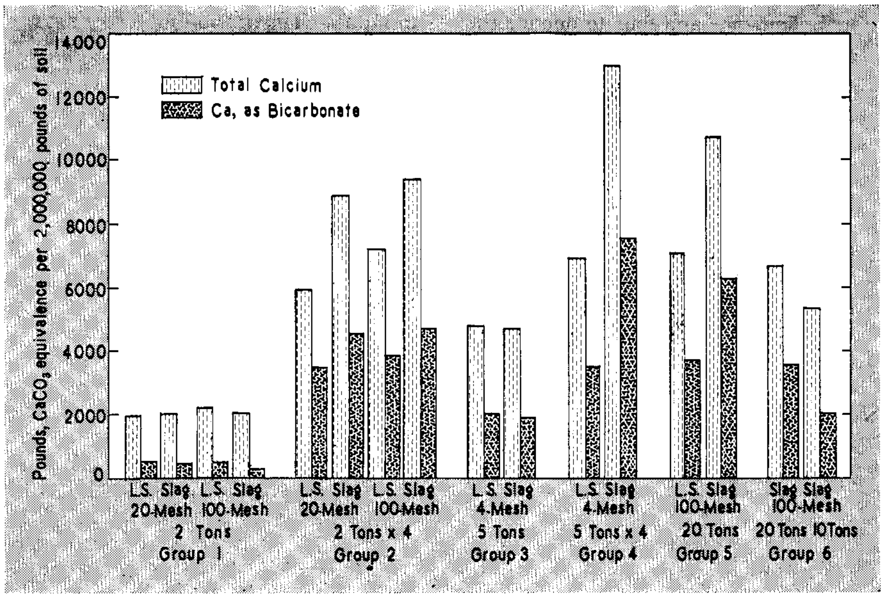


Figure 2. Calcium leached, total and as bicarbonate, in 10 years

From equivalent incorporations of silicote slag and limestone in Hartsells fine sandy loam. Full depth in groups 1–5; half depth in group 6

soils. In both 5-year periods, calcium outgo from the 20-ton incorporation of slag in the upper half of soil was decidedly less than the outgo of calcium from the corresponding full-depth incorporations.

Net outgo of calcium from the two fallow soils might have been considerably different had the soils been cropped in the two 5-year periods. Biological activities would have caused increases in the calcium content of free water in the soils, but those increases would have been diminished through uptake by the vegetation, and the quantity of the drainage and concentration of its solutes would be lessened. Incorporations of liming materials at rates beyond 2 tons of calcium carbonate equivalence per acre are likely to increase the calcium content of drainage waters and cause wastage of calcium from soils of the types under study.

The increases in calcium outgo were expressed as though they were derived entirely from the additive materials. However, through use of radioactive calcium-45 as a component of calcium carbonate incorporations in two soils, it was found that enhancement in the calcium content of rain-water drainage from a limed soil may come partly from native supplies and that outgo of calcium from those supplies in a particular soil may be diminished or increased through variation in the rate of calcium input (*2*, *3*).

Bicarbonate leachings from the slagged and limestoned Hartsells and Baxter soils are reported in Tables VI and VII. Each net increase in 10-year passage of bicarbonates is designated "outgo increase." Although the two rock-derived soils are decidedly acidic and devoid of determinable contents of carbonates, their leachings usually carry measurable quantities of bicarbonate.

Increases in bicarbonate from the single 2-ton inputs in the two soils were from 300 to 500 pounds against a 4109-pound mean increase from the eight units that received the four 2-ton annual incorporations, as in groups 1 and 2 of Tables VI and VII. In every comparison, bicarbonate outgo from the slagged soil exceeded that from the correspondingly limestoned soil.

Upon assumption that like quantities of carbonate were engendered from the 20-ton inputs of slag in the upper zone and in full depth of the soils of groups 5 and 6 of Tables VI and VII, bicarbonate outgo from the upper zone of soil (group 6) was diminished substantially, as was total calcium outgo (Tables III and IV), through the stoppage in the lower zone of unslagged soil.

The bicarbonates that passed from the heavily limestoned soils probably came chiefly from the portions of limestone that had not been decomposed by the soil. Only one unit of carbon dioxide was required to convert a unit of solid phase calcium carbonate into a bicarbonate solute, whereas two units of carbon dioxide in the much larger passages of bicarbonate were required for the engendering of each unit of calcium carbonate and sequential formation of solute carbonate from the slag, as indicated by the equation,

$$CaSiO_3 + 2H_2O \rightarrow Ca(OH)_2 + H_2O + SiO_2 \quad (1)$$

$$Ca(OH)_2 + H_2X \rightarrow CaX + 2H_2O \rightarrow \text{sorbed} \quad (2)$$

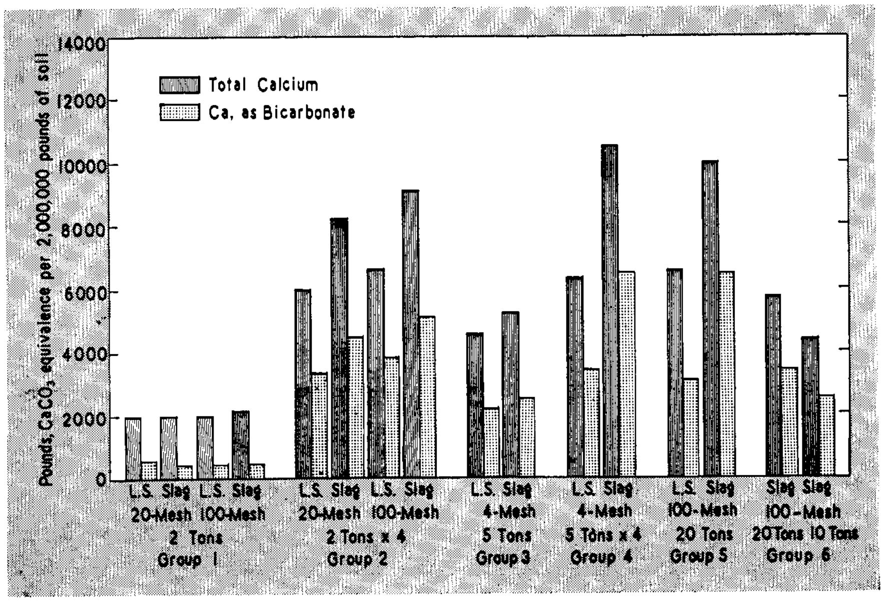
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \rightarrow \text{precipitate} \quad (3)$$

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \rightarrow \text{solution} \rightarrow \text{outgo} \quad (4)$$

The percentage of carbonate in a calcium-fortified soil at a given time will be governed by the degree of acidity that prevailed in the soil before the incorporation of the liming material; by rate, type, and sizing of the incorporated liming material; by the extent and periodicity of rainfall; by variations in biological activities under different seasonal conditions; and probably by geochemical "aging" in the interval between the incorporation and the sampling of the calcium-enriched soil. Where the acidoids and the carbon dioxide of a slagged soil system are in competition for the calcium hydroxide that is engendered through hydrolysis of the calcium silicate of the slag, the fate of small inputs of slag will be chiefly that of Equation 2, whereas Equations 3 and 4 represent what happens to those quantities of

Figure 3. Calcium leached, total and as bicarbonate, in 10 years

From equivalent incorporations of silicate slag and limestone in Baxter silt loam. Full depth in groups 1–5; half depth in group 6



engendered hydroxide that do not undergo sorption directly by the soil acidoids.

The reaction indicated by Equation 2 is reversible through hydrolysis of the $CaX + 2H_2O \rightarrow Ca(OH)_2 + H_2X$ and may impart determinable quantities of bicarbonate to the soil leachings, as indicated by Equations 3 and 4 in sequence, even when analysis of the soil may show it devoid of solid phase carbonate. However, the calcium silicate of one phosphate furnace slag may undergo hydrolysis and carbonation readily, whereas another slag of like appearance may not. Moreover, the reactivity imparted through the quenching of the molten slag may be very different from the reactivity of the air-cooled crystalline slag.

Induced Changes in Soil pH

After 10 years, a pH value of 6.3 was common to the four units of each of the Hartsells and Baxter soils that received the 2-ton incorporations (group 1 in Tables III and IV). In most cases, the final pH values induced by the two liming materials were virtually identical for the rational-rate incorporations. The eight corresponding units that received the four 2-ton-per-annum incorporations showed a pH mean of 7.7; the 5-ton incorporations of 4-mesh materials registered final pH values of 7.1 against respective values of 7.9 to 8.4 for the four 5-ton annual inputs, and the 20-ton single incorporations registered a mean pH value of 8.2.

Carbonate Residues

None of the 2-ton incorporations in the eight soil systems of group 1 (Table VIII) resulted in a carbonate residue. Although bicarbonate leachings accounted for as much as 65% of net outgo from

Table VI. Calcium Bicarbonate Outgo in 10-Year Rain-Water Leachings from Equivalent Incorporations of Limestone and Slag in Hartsells Fine Sandy Loam

	Incorporations[a]				Annual Outgo, Pounds $CaCO_3$ Equivalence per Acre, 2,000,000 Pounds of Soil											
Group	Materials	Mesh	Tons	No.	1	2	3	4	5	6	7	8	9	10	Total	Outgo Increase[b]
	None	...	...	.	53	98	81	79	169	113	91	88	132	169	1073	...
1	Limestone	20	2	1	71	200	146	146	176	163	107	111	165	186	1471	398
	Slag	20	2	1	56	161	129	148	184	148	106	104	158	184	1378	305
	Limestone	100	2	1	72	198	144	150	203	135	103	101	158	176	1440	367
	Slag	100	2	1	66	165	140	151	182	143	106	106	162	178	1399	326
2	Limestone	20	2	4	58	363	485	518	524	376	326	272	396	501	3819	2746
	Slag	20	2	4	61	342	824	1008	803	632	505	446	491	520	5632	4559
	Limestone	100	2	4	75	512	508	589	650	598	501	403	500	622	4958	3885
	Slag	100	2	4	63	447	1222	939	801	639	516	400	384	428	5839	4766
3	Limestone	4	5	1	98	311	368	417	431	353	271	206	311	366	3132	2059
	Slag	4	5	1	91	355	397	353	323	352	267	213	308	302	2961	1888
4	Limestone	4	5	4	93	460	564	555	595	428	381	389	476	608	4549	3476
	Slag	4	5	4	103	1071	1010	954	1103	800	891	814	858	1058	8662	7589
5	Limestone	100	20[c]	1	210	510	478	484	535	516	524	368	527	673	4825	3752
	Slag	100	20[c]	1	438	964	917	950	824	755	563	505	724	793	7433	6360
6	Slag	100	20[c]	1	73	307	369	335	465	609	502	517	693	768	4638	3565
	Slag	100	10[c]	1	67	259	290	256	332	418	291	222	462	545	3142	2069
	Rainfall, inches				31.85	41.06	57.88	51.19	55.60	53.81	50.98	42.69	56.57	62.60	504.23	

[a] Basis of $CaCO_3$ equivalence. Full-depth incorporations for groups 1–5; half-depth for group 6.
[b] Net losses in relation to inputs.
[c] Soil undisturbed during 10 years.

Table VII. Calcium Bicarbonate Outgo, in 10-Year Rain-Water Leachings from Equivalent Incorporations of Limestone and Slag in Baxter Silt Loam

	Incorporations[a]				Annual Outgo, Pounds $CaCO_3$ Equivalence per Acre, 2,000,000 Pounds of Soil											
Group	Materials	Mesh	Tons	No.	1	2	3	4	5	6	7	8	9	10	Total	Outgo Increase[b]
	None	...	..	...	39	80	72	91	160	106	90	85	129	150	1002	...
1	Limestone	20	2	1	66	223	156	231	190	146	117	101	160	184	1574	572
	Slag	20	2	1	51	173	141	149	165	141	122	113	168	190	1413	411
	Limestone	100	2	1	61	205	141	161	186	145	125	118	174	193	1509	507
	Slag	100	2	1	56	175	121	169	199	146	114	116	179	197	1472	470
2	Limestone	20	2	4	53	456	415	562	551	447	459	435	489	536	4403	3401
	Slag	20	2	4	55	350	705	942	789	595	515	512	467	548	5478	4476
	Limestone	100	2	4	59	495	533	567	669	509	500	426	496	603	4857	3855
	Slag	100	2	4	63	537	1000	916	820	783	559	464	449	598	6189	5187
3	Limestone	4	5	1	71	329	315	442	363	374	328	260	316	408	3206	2204
	Slag	4	5	1	116	473	442	331	459	352	307	279	344	448	3551	2549
4	Limestone	4	5	4	79	431	458	496	577	531	412	444	475	638	4541	3539
	Slag	4	5	4	110	856	733	830	995	850	762	705	686	886	7413	6411
5	Limestone	100	20[c]	1	135	435	524	416	465	474	356	302	459	609	4175	3173
	Slag	100	20[c]	1	501	847	884	912	750	691	676	452	650	960	7323	6321
6	Slag	100	20[c]	1	67	194	366	366	531	551	498	449	609	845	4476	3474
	Slag	100	10[c]	1	46	131	287	277	382	514	448	319	492	710	3606	2604
	Rainfall, inches				31.85	41.06	57.88	51.19	55.60	53.81	50.98	42.69	56.57	62.60	504.23	

[a] Basis of $CaCO_3$ equivalence. Full-depth incorporations for groups 1–5; half-depth for group 6.
[b] Net losses in relation to inputs.
[c] Soil undisturbed during 10 years.

the four 2-ton annual incorporations in the corresponding slagged systems of the two soils of group 2 (Table VIII), the carbonate residues from the slag were small. The largest residual occurrence of calcium carbonate from the four 2-ton annual incorporations of 100-mesh slag was the one of only 700 pounds in the Hartsells soil (Table VIII), as the ultimate result from two phenomena—soil fixation of calcium of the slag and the leachings of biologically induced solutes of calcium.

Although outgo of bicarbonate from each slag input in group 3 of Tables VI and VII was larger than the bicarbonate outgo from its limestone equivalent, there were no accumulations of calcium carbonate from the two slagged soils, as detailed under "increase engendered" in Table VIII.

In both soils, maximal residues of slag-derived carbonate were those engendered from the 20-ton inputs of the 100-mesh separate. Respective combinations of the 16,600-pound and 17,500-pound "soil carbonate, increases engendered" and the corresponding 10,706-pound and 10,049-pound leachings of calcium carbonate account for aggregates of 27,306 and 27,549 pounds of slag-derived calcium carbonate from the 20-ton full-depth inputs of slag in Hartsells and Baxter soils (Table VIII). These aggregates are equivalent to 68.3 and 68.9% of the calcium carbonate potential of the incorporated 20-ton input of slag, but they do not include the calcium carbonate equivalences of the calcium that effected displacements of hydrogen ions in the two soils. Upon the basis of difference between the decomposition of the incorporated limestone and the leachings therefrom, it appears that the replacement of Ca^{++} for $2H^+$ accounted for 8612 and 8770 pounds of calcium carbonate in the Hartsells and Baxter soils, respectively. In case of equal replacement of hydrogen by the calcium of the slag, the silicate transitions of 68.3 and 68.9% are raised to 89.8 and 90.8% for Hartsells and Baxter soils, respectively.

Effects of Silicate Calcium upon Outgo of Other Soil Components

The 10-year leachings of seven elements from the six groups of the experimentally slagged and limestoned units of each soil are given in Table IX.

Magnesium outgo was lessened from every soil system of the 32 units into which calcium had been incorporated and the repressions of leachings of magnesium were accentuated by the larger rate incorporations of both liming materials.

Potassium outgo from stores native to the soil was repressed by every incorporation of each liming material. Repressions of potassium outgo were accentuated by the larger incorporations of both limestone and slag; but the repressive effects exerted by the larger incorporations of slag were offset somewhat by the quantities of potassium those incorporations brought to the soil—up to 109 pounds of K_2O per acre.

The invariable repression in the outgo of potassium in the rain-water leachings from the slagged and limestoned soils are in accord with findings obtained many times at this station and at the Virginia station (*20*). But, as noted by Kelley (*4*), the purported opposite effect is still a contention. In recent bulletins from those two stations (*20*), an attempt was made to rationalize the potassium repressions into a base interchange concept that an incorporation of an alkaline calcic, magnesic, or dolomitic material will cause a decrease in the quantity of potassium that a soil will yield to its rain-water drainage.

Fluorine in Drainage Waters

The behavior and leachability of the fluorine of the incorporated slag are distinctive from the behavior of the fluorine of corresponding incorporations of calcium fluoride and other fluorides (*8*, *9*). The mean increase in 10-year outgo of fluorine from the 2-ton incorporations of slag (group 1 of Table IX) was only 31 pounds per acre, whereas mean increases of 511 and 427 pounds in the outgo of fluorine were induced by the four 2-ton annual incorporations (group 2) in the Hartsells and Baxter soils, respectively.

The largest outgo of fluorine was that of 810 pounds, which passed from the 20-ton full-depth incorporation of slag in the Hartsells soil and represented 80% of the quantity carried by the slag. In case the 810-pound leachings had been made to pass through an underlying stratum of untreated soil or subsoil, the

Table VIII. Relationships of Net Total Leachings of Calcium to Proportions Leached as Calcium Carbonate from Equivalent Inputs of Limestone and Slag and to Final Soil Carbonate Content

(Decreases or increases after 10 years)

	Incorporations[a]				Hartsells Fine Sandy Loam						Baxter Silt Loam					
					Net Outgo of Ca						Net Outgo of Ca					
							Carbonate		Soil Carbonate, Lb.				Carbonate		Soil Carbonate, Lb.	
Group	Materials	Mesh	Tons	No.	Total, lb.	Of input, %	As such, lb.	Of input, %	Decrease from input	Increase engendered	Total, lb.	Of input, %	As such, lb.	Of input, %	Decrease from input	Increase engendered
1	Limestone	20	2	1	1966	49	398	9	4,000	...	2102	53	572	14	4,000	...
	Slag	20	2	1	2084	52	305	8	...	0	2082	52	411	10	...	0
	Limestone	100	2	1	2262	57	367	9	4,000	...	2121	53	507	13	4,000	...
	Slag	100	2	1	2115	53	326	8	...	0	2231	56	470	12	...	0
2	Limestone	20	2	4	5901	37	2746	17	12,300	...	6017	38	3401	21	12,000	...
	Slag	20	2	4	8986	56	4559	30	...	200	8282	52	4476	28	...	400
	Limestone	100	2	4	7221	45	3885	24	14,200	...	6641	42	3855	24	13,500	...
	Slag	100	2	4	9448	59	4766	30	...	700	9065	57	5187	32	...	600
3	Limestone	4	5	1	4787	48	2059	21	9,400	...	4579	46	2204	22	9,200	...
	Slag	4	5	1	4774	48	1888	19	...	0	5218	52	2549	25	...	0
4	Limestone	4	5	4	6959	17	3476	9	17,400	...	6370	16	3539	9	14,900	...
	Slag	4	5	4	13053	33	7589	19	...	8,100	10554	26	6411	16	...	8,500
5	Limestone	100	20[b]	1	7088	18	3752	9	15,700	...	6430	16	3173	8	15,200	...
	Slag	100	20[b]	1	10706	27	6360	16	...	16,600	10049	25	6521	16	...	17,500
6	Slag	100	20[b]	1	6687	17	3565	9	...	18,250	5778	14	3474	9	...	19,950
	Slag	100	10[b]	1	5289	26	2069	5	...	5,500	4551	23	2604	13	...	6,500

[a] Per 2,000,000 pounds of soil, moisture-free basis; full-depth incorporations for groups 1–5; half-depth for group 6.

[b] Soil undisturbed during 10 years.

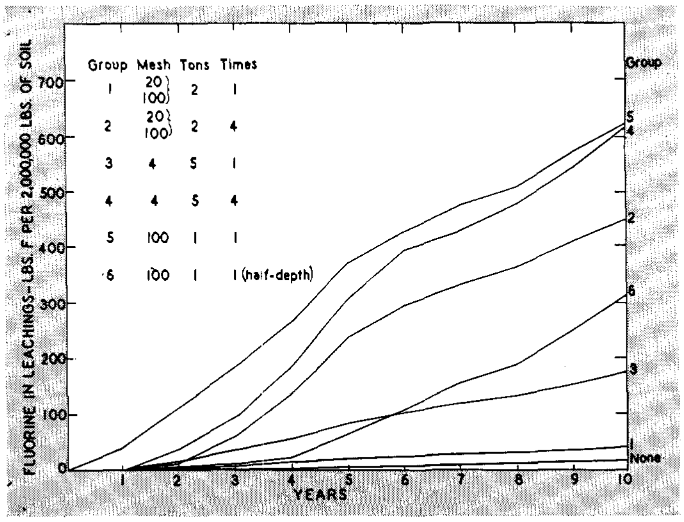


Figure 4. Fluorine leachings in 10 years

From Hartsells fine sandy loam after incorporations of quenched calcium silicate slag of three finenesses and at several rates (Table IX)

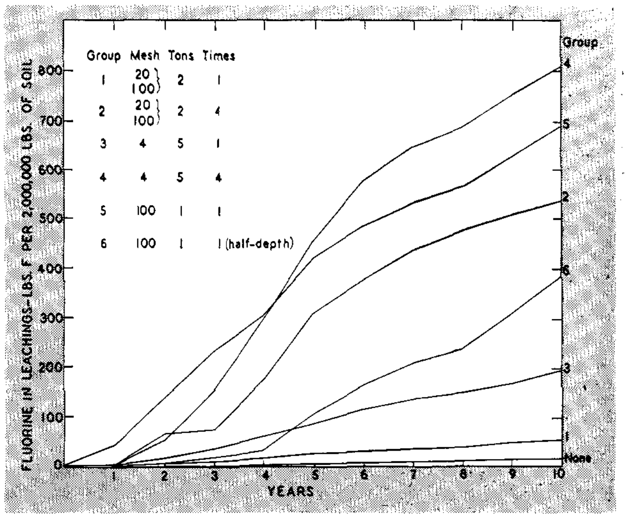


Figure 5. Fluorine leachings in 10 years

From Baxter silt loam after incorporations of quenched calcium silicate slag of three finenesses and at several rates (Table IX)

concentration of solute fluorides would have been decreased by half. Such stoppage was registered by the differences between the leachings of fluorine from the 20-ton incorporations of slag at the two depths in both soils, as in groups 5 and 6 of Table IX. The high concentrations of fluorides in the leachings from the heavily slagged soils were accompanied by large increases in the outgo of solvated silica and calcium solutes. Because the simple fluoride (CaF_2) does not leach from the soil so readily (*8*, *9*), it appears that the large outgo of fluorine from the slagged soils is attributable to leachings of calcium silicofluoride ($CaSiF_6$) (*11*). In case the fluorine and phosphorus contents of the slag are in combinations with silica, before and/or after the slag undergoes disintegration in the soil, a plausible explanation follows as to why the occurrences of fluorine and phosphorus in the rain-water leachings from the slag were so much greater than the occurrences of those two elements in the leachings from jointly incorporated calcium fluoride and calcium phosphate in related experiments (*8*, *9*).

When the reported findings and results are integrated with those obtained in related experiments, it is concluded that rational-rate incorporations of the quenched calcium silicate slag under study would not impart harmful concentrations of fluorides in the drainage waters from the "heavy" types of soils. Moreover, incorporations of that slag at economic rates do not cause an abnormal content of fluorine in resultant crops (*6*, *12*, *13*, *15*).

Summary

A readily hydrolyzable phosphate furnace slag and limestone were compared in a 10-year lysimeter experiment as to fineness, rates, single and repeated inputs, and depth of incorporation in two major soils.

Rainwater increments and leaching effects upon exchangeable bases, exchange capacities, and soil pH values were determined.

After 10 years, the eight systems that received single 2-ton full-depth incorporations of 20- and 100-mesh slag and limestone had lost half of the calcium input, a fifth of the outgo being calcium bicarbonate, were devoid of calcium carbonate, and had pH values of 6.3.

The three additional annual inputs of 2 tons in the two soils caused 3- to 4-fold increases in calcium, half of the increases being bicarbonates, and leachings of calcium from slag-engendered carbonate were far greater than those from the corresponding inputs of limestone. The four systems that received four 2-ton incorporations of 20- and 100-mesh slag contained slag-derived calcium carbonate residues of only 200 to 700 pounds per acre, although those systems had yielded 4.5 tons of calcium carbonate to the 10-year drainage.

The repetitive incorporations and larger inputs of both liming materials caused further increases in calcium outgo, the leachings of calcium from the larger inputs of the slag being substantially greater than those from the equivalent inputs of limestone.

Because of sorption and leachings of the calcium from the slag of the 5-ton inputs of 4-mesh slag, there were no accumulations of calcium carbonate, as indicated in the eleventh column of Table VIII, although those inputs had yielded almost 2.5 tons of calcium carbonate to the leachings from each soil, half of each total outgo being bicarbonate.

In the initial year, the largest leachings of calcium were from the full-depth 20-ton incorporations of 100-mesh slag; but the four 5-ton annual inputs of 4-mesh slag gave largest 10-year outgo from both soils.

Total and bicarbonate leachings of calcium from undisturbed soils that received 20-ton full-depth incorporations of 100-mesh slag were almost twice the leachings from the corresponding incorporations at half-depth.

In 10 years sorption and leaching jointly caused a mean decrease of 15,450 pounds of calcium carbonate from the 20-ton incorporations of limestone in the two soils, against which were gains of 17,050 and 19,100 pounds of calcium carbonate from the equivalent incorporations of slag in full depth and in the upper half of soil.

Final pH values for the eight systems that received single 2-ton incorporations of slag and limestone were 6.3; for the 5-ton incorporations of the 4-mesh materials, 7.1 in the two; and for the repetitive and heavy-rate incorporations, from 7.7 to 8.4.

Magnesium and potassium appearances in the drainage waters were repressed by all incorporations of slag and of limestone in both soils. The repressions exerted by the 20-ton inputs in the twelve units of groups 4, 5, and 6 were especially significant (Table IX). Because of the offsetting effect of its content of potassium, the slag appeared to be less repressive than limestone upon outgo of that element.

Nitrate leachings and sulfate outgo were increased by the inputs of both liming materials. In all cases, the larger outgo of sulfates was induced by the slag, each ton of which contained 5.8 pounds of sulfur.

The occurrences of fluorine and phosphorus in the incorporated slag were reflected by the enhancements in leachings from slagged soils. Largest outgo of fluorine was the 810-pound leaching from the four annual 5-ton incorporations of 4-mesh slag in Hartsells soil, and represented a 52% recovery of the quantity carried by the four 5-ton inputs. The mean outgo of fluorine from the 20-ton upper-zone incorporations of 100-mesh slag was only 53% of the outgo from corresponding full-depth incorporations.

Incorporated slag yielded calcium hydroxide readily and fractions not sorbed directly by the soil then were converted to calcium carbonate, up to an engendered residue of 19,950 pounds; proved more reactive than the limestone; was leached sooner and to greater extent; registered less repression than limestone upon outgo of potassium and magnesium; imparted some of its phosphorus content to the drainage waters; and yielded relatively small outgo of fluorine from the rational-rate inputs. However, the 10 years' drainage from the 20-ton incorporations yielded up to 53% of their 1524-pound content of fluorine.

Because of the porosity and particulate nature of the slag, its larger particles proved more reactive than limestone of decided fineness.

Conclusions

Comparable effects were induced by the calcium of rational-rate incorporations of phosphate furnace slag and limestone, but decidedly different effects ensued when equivalent quantities of the two materials were compared by means of repetitive incorporations and by single inputs at heavy rates.

Although the repetitive and the large single inputs of slag yielded calcium leachings decidedly greater than those from the limestone, there were substantial cumulations of slag-derived calcium carbonate.

The findings indicate that rational-rate incorporations of a good quenched phosphate furnace slag can be utilized effectively as an economic liming material without qualification other than that it be incorporated, and its use will not cause detrimental concentrations of fluorine in the waters of nearby wells and streams.

Acknowledgment

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Table IX. Ten-Year Outgo of Calcium, Magnesium, Potassium, Phosphorus, Sulfur, Nitrogen, and Fluorine from Equivalent Incorporations of Limestone and Slag[a]

(Pounds per acre)

	Incorporations[a]				*From Hartsells Fine Sandy Loam*							*From Baxter Silt Loam*						
Group	*Materials*	*Mesh*	*Tons*	*No.*	*Ca*	*Mg*	*K*	*P*	*S*	*N*	*F*	*Ca*	*Mg*	*K*	*P*	*S*	*N*	*F*
	None	. . .	. .	. . .	803	201	55	1.0	534	355	14	795	227	119	0.6	564	394	14
1	Limestone	20	2	1	1591	143	29	0.8	580	458	18	1636	182	99	0.6	622	560	15
	Slag	20	2	1	1638	156	34	1.2	614	487	48	1628	179	92	0.7	655	531	36
	Limestone	100	2	1	1709	147	32	0.9	601	530	17	1644	177	100	0.7	644	566	13
	Slag	100	2	1	1650	161	30	1.3	646	506	52	1688	188	84	1.0	655	526	43
2	Limestone	20	2	4	3167	100	24	1.1	628	669	25	3204	151	71	0.8	694	586	22
	Slag	20	2	4	4402	104	30	2.1	697	652	529	4111	128	74	1.3	744	592	452
	Limestone	100	2	4	3695	85	18	1.0	666	622	26	3454	133	67	0.8	669	580	18
	Slag	100	2	4	4587	121	30	2.3	730	623	542	4424	150	70	1.4	748	572	446
3	Limestone	4	5	1	2720	128	20	1.0	621	628	22	2628	151	72	0.7	664	571	22
	Slag	4	5	1	2715	123	24	1.2	635	560	190	2884	155	83	0.7	712	530	172
4	Limestone	4	5	4	3590	99	16	1.1	674	693	23	3345	139	72	0.9	694	596	17
	Slag	4	5	4	6031	98	41	3.6	760	687	810	5021	113	82	1.9	759	632	618
5	Limestone	100	20[b]	1	3642	42	19	1.0	659	664	24	3369	72	67	1.0	678	614	22
	Slag	100	20[b]	1	5091	73	45	3.6	692	482	687	4818	116	79	4.3	720	494	627
6	Slag	100	20[b]	1	3481	87	30	0.8	712	583	383	3108	147	77	0.9	701	508	315
	Slag	100	10[b]	1	2922	80	27	0.8	733	613	279	2617	125	58	0.6	636	410	222
	Mean of variations[c]			*d*	. .	−95	−32	0	+99	+254	+8	. .	−84	−44	+0.2	+102	+188	+4
				e	. .	−82	−22	+2.2	+148	+216	+394	. .	−28	−38	+1.0	+149	+160	+328

[a] In $CaCO_3$ equivalence per acre, 2,000,000 pounds of soil, m.f. basis.
[b] Soil undisturbed 10 years.
[c] In 10-year totals for full-depth groups 1–5.
[d] Effects induced by limestone.
[e] Effects induced by slag.