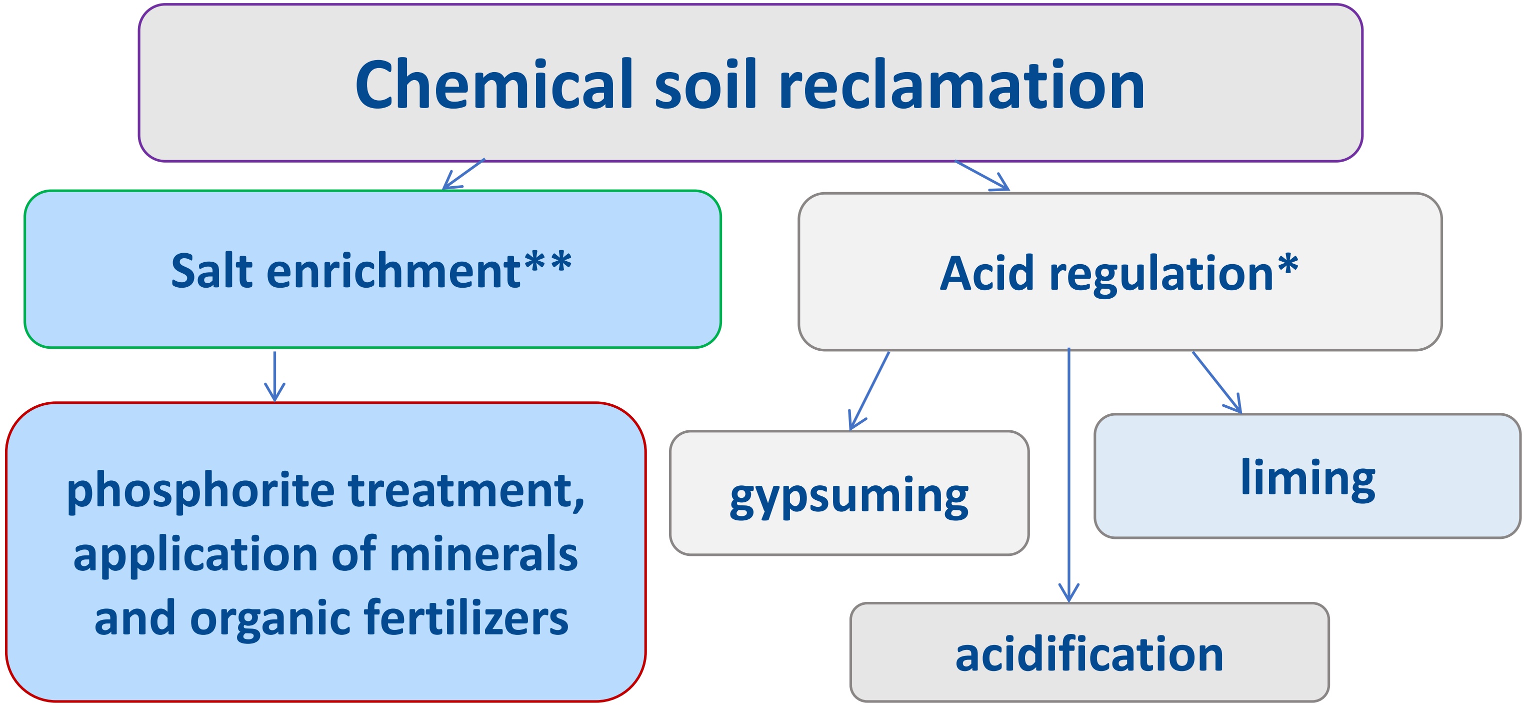
PROAGRO LECTORIUM

How calcium affects soil acidity

Doctor of Biological Sciences N.I. Akanova



According to Food and Agriculture Organization's forecasts, the world demand for mineral fertilizers is currently at least 300 million tons of nutrients (170N, 70P, 60K). Global production is 204 million tons by 2020. 25 billion tons of organic fertilizers are applied worldwide.

*measures to create a favorable response of the soil medium
**measures to increase the content of essential nutrients in the soil

A key parameter of soil fertility is the response of the soil medium. Soils saturated with Ca and Mg (black soils) have a neutral or slightly acidic response; soils not saturated with bases are characterized by an acidic response. Soddy-podzolic and gray forest soils are characterized by an acidic response of the medium. The soil medium response is expressed by the pH value, which characterizes the concentration of hydrogen ions in it. The lower the pH, the higher the soil acidity:

extremely acidic	....	< 4.0
Strongly acidic	....	4.1–4.5
Medium acidic	....	4.6–5.0
Slightly acidic	....	5.1–5.5
Close to neutral	....	5.6–6.0
Neutral	....	6.0
Alkaline	....	7–8

Liming is a method for chemical reclamation of acidic soils, which means applying lime fertilizers to them. The effect of liming is determined by the substitution of hydrogen and aluminum ions in the soil-absorption complex for both calcium and magnesium contained in the fertilizer.

The physiological (biological) optimum of the medium response for plants differs from **the ecological** (technological) one, relating to the mobility of nutrients and the conditions for the development of diseases.

Thus, for potato and flax plants, if the soil is not infected, the biological optimum is pH_{KCl} 6.0–6.2 but, when infected (potatoes with a neutral and slightly alkaline response are affected by scab caused by actinomycetes, flax — by fusarium), in fields, the yield and quality of these crops are higher at pH_{KCl} 5.2–5.6, that is, at an ecological optimum.

The discrepancy between the biological and ecological optimum of the medium response for many crops is caused by changes in the availability of nutrients when the pH of the soil changes.

Here, changes in the availability of macro- and micronutrients when liming should be considered. Liming of soil with a pH above 6.6 is useless, since the removal and leaching of calcium from the soil increases and the mobility of microelements, excluding molybdenum, decreases.

Optimal medium response for different soil microorganisms

Main physiological groups of microorganisms	Name of microorganisms	Optimal pH values	Bottom line pH
Nitrogen fixers binding the air molecular nitrogen	Symbiotic (nodule):		
	alfalfa	6.8–7.2	4.9–5.0
	clover	6.8–7.2	4.2–4.7
	peas and vetch	6.5–7.0	4.0–4.7
	lupine and seradella	5.5–6.5	3.2–3.5
	Free living:		
	azotobacter	6.5–7.5	5.5–6.0
	clostridium	5.0–7.0	4.7–5.0
Microorganisms decomposing plant debris	Mushrooms	4.0–5.0	1.5–2.0
	Butyric acid bacteria	6.5–7.0	4.5–5.5
	Cellulose-destroying	6.2–7.2	–
	Ammonifiers	6.2–7.0	–
	Denitrifiers	7.0–8.0	6.0–6.2
Microorganisms mineralizing humic substances	Nitrifiers	6.5–7.5	4.8–5.0
	Phosphorus mobilizers	6.5–7.5	–

Calcium carbonate loss from light loamy soil with a lime requirement of 5 t/ha for 15 years

Years	$CaCO_3$, t/ha, added					
	12.6		6.3		3.1	
	Annual loss of $CaCO_3$, kg/ha and soil pH					
	losses	pH	losses	pH	losses	pH
0–5	1000		630		380	
5–10	500	6.5–6.0	310	5.5–6.0	190	5.0–5.5
10–15	250	5.5–6.0	130	5.0–5.5	60	4.7–5.5
	Total losses of $CaCO_3$, t/ha for 15 years					
	8.8		5.3		3.1	

Annual losses of $CaCO_3$, kg/ha = 1920 – 702 pH + 74 pH^2

The influence of different forms of nitrogen fertilizers on the loss of calcium and magnesium from soil with filter sediments, kg/ha

Option	Ca	Mg
PK	326	87
PK + $CO(NH_2)_2$	248	79
PK + $NaNO_3$	257	75
PK + $(NH_4)_2SO_4$	799	203

Among the factors strongly influencing the quantitative parameters of calcium and magnesium losses, there are **doses and forms of nitrogen fertilizers**. The application of **ammonium sulfate increased the loss of calcium and magnesium by 2.5 times**

Calculation of the $CaCO_3$ content (t/ha) is made based on the value of hydrolytic acidity (H) according to the formula
$P_{CaCO_3} = H \bullet 0.05 \bullet h \bullet d$,
where h is the thickness of the cropland layer, d is its density.
The $CaCO_3$ dose (t/ha) can also be calculated approximately based on the pH value of the salt, considering the soil's particle size structure.

Particle size structure	pH of salt extract					
	< 4.5	4.6	4.8	5.0	5.2	5.4–5.5
Sandy	2.5	2.1	1.6	1.3	1.0	0.7–0.5
Sandy loam	3.5	3.0	2.5	2.0	1.5	1.2–1.0
Light loamy	4.5	4.0	3.5	3.0	2.5	2.0
Medium loamy	5.5	5.0	4.5	4.0	3.5	3.0
Heavy loamy	7.0	6.5	6.0	5.5	5.0	4.5
Clayey	8.0	7.5	7.0	6.5	6.0	5.5

Recommended optimal acidity levels of cropland soil layer (pH_{KCl})

Particle size structure of soils	Crop rotations		Cultivated pastures and hayfields	
	Fields	Forages	Cereals	Cereals-and-legumes
Sandy and sandy loam	5.3–5.5	5.5–5.7	5.2–5.4	5.4–5.6
Light and medium loamy	5.6–5.8	5.6–6.0	5.4–5.6	5.6–5.8
Heavy loamy and clayey	5.8–6.0	6.0–6.2	5.6–5.8	6.0–6.2
Peat-bog soils	4.8–5.2	5.2–5.4	4.6–4.8	5.0–5.2

Recommended doses of $CaCO_3$ for a shift of 0.1 pH_{KCl}

Soil type	Initial soil pH_{KCl} value	$CaCO_3$ consumption (t/ha) to shift pH_{KCl} by 0.1
Cropland		
Soddy-podzolic, gray forest, podzolized and leached black soils	< 4.5	0.75
	4.6–5.0	0.91
	5.1–5.5	1.30
	> 5.6	1.95

$CaCO_3$ need for neutralization of nitrogen fertilizers during their application (tons/ton)

Name of the fertilizer	Chemical formula	Nitrogen content (%)	$CaCO_3$ mass, t
Ammonium sulfate	$(NH_4)_2SO_4$	21.1	1.2
Ammonium chloride	NH_4Cl	26.1	1.4
Ammonium nitrate	NH_4NO_3	35.0	1.0
Ammonium bicarbonate	NH_4HCO_3	17.5	0.44
Urea	$CO(NH_2)_2$	46.5	1.2
Ammonia water	NH_4OH	20.5	0.51

$CaCO_3$ doses for soils in the Central region of the zone without black soils, t/ha

Soils	pH_{KCl}									
	3.8–3.9	4.0–4.1	4.2–4.3	4.4–4.5	4.6–4.7	4.8–4.9	5.0–5.1	5.2–5.3	5.4–5.5	5.6–5.8
Sandy	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.2	1.0	–
Sandy loam	7.0	5.5	4.5	3.5	3.0	2.5	2.0	1.5	1.2	–
Light loamy	8.0	6.5	5.5	4.5	4.0	3.5	3.0	2.5	2.5	1.5
Medium loamy	9.0	8.0	6.5	5.5	5.0	4.5	4.0	3.5	3.0	2.5
Heavy loamy	10.5	9.5	7.5	6.5	6.0	5.5	5.0	4.5	4.0	3.0
Clayey	12.5	10.5	9.0	7.0	6.5	6.0	5.5	5.0	4.5	3.5

Physical and chemical parameters of limestone (dolomite) meal, grade A (GOST 14050-93)

Parameter name		Class 1	Class 2	Class 3	Class 4
Strength of initial carbonate rock in compression in water saturated state		Less than 20 MPa	Up 20 to 40 MPa	Up 40 to 60 MPa	Up 60 MPa
Total mass fraction of calcium and magnesium carbonates, %, NLT		80	80	85	85
Grain composition, %, total residues on sieves	NMT 5 mm	0	0	0	0
	NMT 3 mm	3*	3	2	1
	NMT 1 mm	25	15	10	3
Mass fraction of moisture, %, NMT	group 1	1.5	1.5	1.5	1.5
	group 2	6.0	6.0	6.0	3.0
Active agent parameter, %, NLT	group 1	78	74	78	81
	group 2	74	71	75	77

*For limestone (dolomite) meal of grade A, class 1 (group 2), the residue on a 3 mm sieve not more than 5% is acceptable

Physical and chemical parameters of limestone (dolomite) meal, grade B (GOST 14050-93)

Parameter name			Class 1	Class 2	Class 3
Strength of initial carbonate rock in compression in water saturated state			Less than 20 MPa	Up 20 to 40 MPa	Up 40 to 60 MPa
Total mass fraction of calcium and magnesium carbonates, %, NLT			80	80	85
Grain composition, %, total residues on sieves		NMT 10 mm	0	0	0
		NMT 5 mm	5	3	2
		NMT 3 mm	10	5	4
		NMT 1 mm	35	25	15
Mass fraction of moisture, %, NMT	no preventive additive	October – March	6.0	6.0	6.0
		April – September	15.0	12.0	8.0
	with preventive additive	October – March	15.0	12.0	8.0
Active agent parameter, %, NLT			64	64	71

Physical and chemical parameters of limestone (dolomite) meal, grade C (GOST 14050-93)

Parameter name			Class 1	Class 2	Class 3	Class 4
Strength of initial carbonate rock in compression in water saturated state			Less than 20 MPa	Up 20 to 40 MPa	Up 40 to 60 MPa	Up 60 MPa
Total mass fraction of calcium and magnesium carbonates, %, NLT			80	80	85	85
Grain composition, %, total residues on sieves		NMT 10 mm	0	0	0	0
		NMT 5 mm	7	5	4	3
		NMT 3 mm	25	20	15	10
		NMT 1 mm	45	40	38	20
Mass fraction of moisture, %, NMT	no preventive additive	October – March	6.0	6.0	6.0	3.0
		April – September	15.0	12.0	8.0	8.0
	with preventive additive	October – March	15.0	12.0	8.0	8.0
Active agent parameter, %, NLT			60	60	60	62

Dolomite meal

Dolomite is a pure mineral, a double calcium-magnesium carbon dioxide salt: $CaCO_3$, $MgCO_3$ at a ratio of CaO: MgO = 1:1.

Dolomite is a sedimentary rock containing slight impurities of carbonic iron and manganese in addition to a double calcium-magnesium salt.

Quality requirements for local lime fertilizers (TU 46-6-77)

Fertilizer	Variety	Neutralizing capacity, % $CaCO_3$, NLT	Moisture contents, %, NMT	Particle size structure (total sieve residue, with cell size), %	
				5 mm	10 mm
Calc-tuff	1	80	30	15	0
	2	70	30	15	0
Lake lime	–	60	30	15	0
Marl clay	–	50	12	15	0
Dolomite meal	–	80	12	15	0

Dependence of $CaCO_3$ decomposition on grinding fineness, % of the applied material

Particle diameter, mm	Undecomposed $CaCO_3$
1.25–2.30	62
0.50–1.25	24
0.125–0.50	17
< 0.125	5

Calculation of the active agent in limestone (dolomite) meal

$$Active\ agent,\ \% = \frac{(100 - I) \cdot (100 - M) \cdot C}{10000},\ where$$

I – content of inactive fractions, %
M – mass fraction of moisture, %
C – total mass fraction of calcium and magnesium carbonates

RUB 1 payback of costs of supporting liming by yield increases of separate crops, RUB.

CROP	$CaCO_3$ DOSES, t/ha			
	2.1	4.2	6.3	8.4
Barley	4.9	4.0	3.5	2.6
Clover (1st year of use)	1.4	1.6	1.7	1.5
Clover (2nd year of use)	0.9	0.9	0.7	0.6
Linen	3.5	3.5	3.4	3.1
Oats	4.1	3.3	2.3	1.7
Potato	5.3	5.2	5.2	4.9
Winter rye	2.1	0.5	2.5	1.5

The agroeconomic efficiency of liming, based on data from research institutions in many countries, is very high.

Each ton of $CaCO_3$ provides a yield increase of about 1 centner of feed units. With increasing anthropogenic load to the entire medium and, in particular, to the soil, chemical reclamation is becoming more and more important as an environment protection factor.

In total, in the first year of operation, the payback of 1 ton of $CaCO_3$ by yield is (c/ha of feed units):

0.93 at pH 4.1–4.5; 0.70 at pH 4.6–5.0 and 0.48 c/ha at pH 5.1–5.5.

The efficiency of potassium fertilizers increases with liming, the prevalence of calcium in the absorbing complex of soils hinders the potassium supply from the soil to plants, and this antagonism is eliminated or weakened with the application of potassium fertilizers. Liming increases potassium absorption by plants, increasing soil potassium depletion.

Soil phosphorus supply also plays a key role in liming efficiency. An increase in available phosphorus shifts the optimal pH to the acidic side.

Effect of liming on crop yields by zone of the region, c/ha

Crop	Yield increase				
	average by region	for soddy-podzolic soils			for gray forest soils
		North-west zone	Central zone		
			West	East	South zone
Winter rye, grain	1.8	1.7	1.7	2.3	–
Oats, grain	2.9	–	2.2	3.1	–
Barley, grain	5.8	2.7	3.6	10.0	1.3
Clover (average over 2 years of use), hay	16.0	17.9	8.8	18.5	5.2

Liming efficiency and dynamics of acidity of leached black soils

NPK, kg/ha	$CaCO_3$, t/ha	Average annual yield c/ha grain units	Increase from lime, c/ha grain units	RUB 1 payback of costs, RUB	pH		Soil acidification, ΔpH	
					Year 1	Year 9	For 9 years	For a year
NPK – 0	0	25.5	–		5.40	5.31	0.09	0.01
	2.6	27.6	2.1	2.99	5.76	5.40	0.36	0.04
	5.2	30.1	4.6	3.24	5.88	5.51	0.27	0.03
$N_{75}P_{90}K_{90}$	0	35.6	–		5.40	5.32	0.08	0.01
	2.6	37.2	1.6	2.34	5.71	5.45	0.26	0.03
	5.2	40.2	4.6	3.24	5.85	5.46	0.39	0.04
	7.8	41.6	6.0	2.86	6.04	5.70	0.34	0.04
	10.4	41.3	5.7	2.10	6.25	5.81	0.44	0.05
$N_{132}P_{150}K_{150}$	0	35.5	–		5.40	5.01	0.39	0.04
	2.6	41.7	2.2	3.12	5.67	5.27	0.40	0.04
	5.2	44.2	4.7	3.30	5.93	5.45	0.48	0.05
	7.8	44.3	4.8	1.75	6.05	5.62	0.43	0.05
	10.4	43.5	4.0	1.51	6.21	5.70	0.51	0.06

Average annual yield increases (t/ha) of grain crops on soddy-podzolic soils of different acidity, depending on the lime dose

Crop	pH_{KCl}	$CaCO_3$ dose, t/ha			
		2–4	4–6	6–8	> 8
Winter wheat	< 4.5	0.39	0.46	0.55	0.66
	4.6–5.0	0.27	0.40	0.46	0.50
	5.1–5.5	0.10	0.15	0.20	0.25
Spring wheat	< 4.5	0.20	0.24	0.26	0.28
	4.6–5.0	0.10	0.15	0.20	0.20
	5.1–5.5	0.05	0.08	0.08	0.10
Barley	< 4.5	0.36	0.40	0.45	0.51
	4.6–5.0	0.30	0.36	0.41	0.44
	5.1–5.5	0.14	0.18	0.20	0.20
Winter rye	< 4.5	0.20	0.23	0.34	0.38
	4.6–5.0	0.17	0.20	0.24	0.28
	5.1–5.5	0.05	0.10	0.12	0.12
Oats	< 4.5	0.20	0.23	0.26	0.29
	4.6–5.0	0.17	0.20	0.22	0.25
	5.1–5.5	0.05	0.10	0.12	0.12

Responsiveness of spring wheat, barley and oats for soil liming, c/ha

Trial option	Spring wheat		Barley		Oats	
	yield	increase	yield	increase	yield	increase
No fertilizers	24.4	–	13.1	–	16.7	–
Liming at 1.0 N_G	25.1	0.7	26.9	13.8	24.9	8.2
NPK	20.2	–	14.1	–	28.5	–
NPK + liming at 1.0 N_G	29.4	9.2	31.7	17.6	31.8	3.3

According to the Geoset's long-term field experiments conducted over 25 years, including long-term field experiment of our institute, the efficiency of phosphorite meal in liming soils varied insignificantly.

Average annual increase by superphosphorite and phosphorite meal for three crop rotations (feed units, c/ha).

Trial option	Yield increase		Increase by phosphorite (Ph), in % to the increase by superphosphorite (SPh)
	from superphosphorite	by phosphorite	
No lime	6.4	6.9	108
With lime	7.1	6.8	92
With lime and manure	4.4	3.4	78

Effect of liming and phosphoritization on grain crops yield (for 5 rotations of crop rotation, c/ha grain units, Institute's field study)

In an Institute's long-term field study, the efficiency of superphosphorite and phosphorite meal were equivalent both on acid soil and under liming conditions (11.2 t/ha CaCO3). Phosphorite meal on soil with a pH of 4.3 increased the yield of winter wheat by 6.8 c/ha, and barley by 9.0 c/ha. When combined with liming, the yield increase almost doubled and the average yield of winter wheat reached 46.1 c/ha and barley — 40.2 c/ha.

Trial option	Winter wheat		Barley	
	yield	increase	yield	increase
NK-background (B)	36.2	–	20.6	–
B + Ph	43.0	6.8	29.6	9.0
B + SPh	40.5	4.3	32.4	11.8
B + $CaCO_3$ 1.5 (main component)	42.1	5.9	30.3	9.7
B + $CaCO_3$ 1.5 (main component) + Ph	46.1	9.9	40.2	19.6
B + $CaCO_3$ 1.5 (main component) + SPh	46.2	10.0	39.2	18.6

Industrial waste rich in lime

1) Shale ash

2) Defecate (defecation slime)

3) Metallurgical slags,

- blast-furnace and open-hearth
- electric-steelmaking and ferroalloy

4) Annealed magnesite

Efficiency of metallurgical slags as chemical ameliorants

Crop	Yield without lime	Yield increase from lime	Yield increase by slag application			
			ferroalloy	electric-steelmaking	open-hearth	
					ground	granular
Spring barley	17.0	2.8	3.2	4.1	2.6	1.8
Winter wheat	26.0	4.2	4.7	4.0	2.9	2.2
Clover (hay)	35.0	14.6	13.2	15.0	12.6	10.8
Maize	283	47	33.5	53	29.5	21.2
Pea-oat mixture (green mass)	124	32	29.1	41	34	28

Metallurgical slags, compared to standard lime fertilizers, have a specific effect on soil and plants, due to the presence of silicic acid in the form of calcium silicate and a large number of trace elements. The effect of slag on soil acidity is weaker than that of natural limestone.

The application return on 1 ton of active agent for metallurgical slag was 14.5 tons of grain units, and for limestone meal was 10.1 tons of grain units.

In summary of the obtained long-term experimental material, it is possible to state that metallurgical slag is among the best forms of lime fertilizers. The main task of its successful application is to prepare these wastes and bring them to the most favorable properties for consumers (neutralizing capacity; particle size, mineralogical, phase and chemical structure).

It is highly prospective to create a lime-phosphorus fertilizer on the MS basis by introducing cheap phosphorite rock into its structure. In this case, the cost price per unit of pentaphosphorus will be 3–4 times lower than in complex fertilizers produced — nitrophoska, azophosk, ammophoska.

Such a complex combination for one application can reduce the need for both lime and phosphorus fertilizers for 8–12 years. The application of potassium will make slag a universal fertilizer.

The significance of slag application as a highly efficient, energy and resource saving factor is actual and extremely prospective.

Thus, the environmental significance of slag application is very important, as not only thousands of hectares of land covered with dumps are freed, but also the soils are enriched with calcium, magnesium, phosphorus, silicon and a complex of microelements.

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