

## Improvement of physical and chemical properties of acidic soils

Okorkov Vladimir Vasilyevich

*Doctor of Agricultural Sciences, Head Research Officer*

*Upper Volga Federal Agrarian Scientific Center*

**Abstract.** When modeling in columns, it was found that a decrease in soil acidity when using dolomite flour occurs due to the neutralization of its agents ( $H^+$  and  $Al^{3+}$  ions) with hydroxyl ions ( $OH^-$ ) formed during alkaline hydrolysis of ameliorant carbonate ions. Instead of neutralized  $H^+$  and  $Al^{3+}$  ions,  $Ca^{2+}$  and  $Mg^{2+}$  ions become exchangeable cations. On strongly and very strongly acidic weakly aggregated soils, in which the bulk of  $H^+$  and  $Al^{3+}$  ions are located on the outer surface of the absorbing complex, the binding of acidity agents by hydroxyl ions occurs at a low concentration of the liquid phase and  $Ca^{2+}$  and  $Mg^{2+}$  ions in it (several mg-eq/l). At the same time, a high effect of some lime-containing ameliorants was observed. On more aggregated strongly, moderately, and weakly acidic soils, exchangeable  $H^+$  and  $Al^{3+}$  ions located on the outer surface of soil aggregates are neutralized by  $OH^-$  ions at a low concentration of the liquid phase (about 4 mg-eq/l  $Ca^{2+}$  and  $Mg^{2+}$ ). The intra-aggregate  $H^+$  and  $Al^{3+}$  ions were displaced from the PPC by high concentrations of divalent cations (several tens of meq/l). The displaced ions, ultimately, were also neutralized by hydroxyl ions due to an increase in the degree of hydrolysis of the carbonate ions of the dissolving ameliorant. The combined use of lime-containing ameliorants and gypsum on more aggregated soils improves the acidic properties deeper than the layer of their introduction and increases the utilization rate of the lime ameliorant.

**Keywords:** illuvial horizons of acidic soddy-podzolic soils, columns, dolomite flour, gypsum, hydrolytic acidity, hydrolysis of carbonate ions, utilization rate of ameliorant.

Soil acidity is a genetic property associated with climate and soil formation conditions on carbonate-free soil-forming rocks, the intensity of agricultural soil use and the ecological state of the environment (biosphere). It increases with the growth of falling and infiltrating precipitation, in areas of technogenic pollution (industrial enterprises for the production of fertilizers, non-ferrous metallurgy enterprises, chemical plants) and acid rain. The intensification of agricultural production has a great influence on it. With the increasing use of mineral fertilizers, soil acidification increases, since the absorption of ammonium and potassium ions, calcium and magnesium cations during plant growth and development occurs in exchange for hydrogen ions, which leads to an increase in

the content of  $H^+$  ions in the soil absorbing complex. In organic and organomineral fertilization systems, the process of soil acidification slows down, but is not completely eliminated.

A noticeable drop in soil fertility is observed when its  $pH_{Cs1}$  falls below 5.3-5.5. In this case, on soils with a low content of organic matter, the content of exchangeable aluminum, mobile forms of iron, sharply increases. manganese, etc. According to the research of N.S. Avdonin [1], when the soil contains 3-5 mg/100 g of mobile aluminum, its toxic effect on the root systems of cultivated crops is observed, their yield may decrease by 30% or more. The content of exchangeable aluminum above the indicated value deeper than the arable layer does not allow the root systems of plants to actively develop and use moisture and nutrients from them during acute and dry periods of crop vegetation, especially during critical ones. Ultimately, this reduces their productivity, the efficiency of the development of intensive technologies for the cultivation of agricultural crops.

Considering the enormous destructive effect of mobile aluminum on the soil, soil biota, cultivated plants, as well as on animals and humans (aluminum disease, sclerosis due to Al accumulation in the brain), it is recommended to include this indicator among the indicators for determining the zones of the ecological state of the soil cover (tab. 1 ). There are zones of ecological norm, ecological risk (areas with a noticeable decrease in productivity, but with the possibility of restoring their ecological stability), ecological crisis (restoration of stability is associated with high costs) and ecological disaster or catastrophe (zones requiring radical improvement). The use of territories of zones of norm and risk should be carried out on the basis of intensive agricultural technologies. To increase the thickness of the root layer, it is important to reduce the acidity of the sub-humus horizons of acidic soils. Reclamation of soils in zones of ecological crisis and disaster should be carried out with the support of the Federal authorities.

Table 1 - Assessment of the ecological state of soils by the content of mobile aluminum, mg/100 g of soil [2]

Acid soil horizons	Ecological zones			
	norms	risk	crisis	disaster
$A_{ARA}$	< 1	1-4	4-8	> 8
Under humus	< 1	> 8	> 8	> 8

To eliminate soil acidity, starting with K.K. Gedroyts, the use of lime fertilizers is generally accepted [1, 3-4].

In 1980, for the chemical reclamation of soils, including acidic soils, mixtures of lime with phosphogypsum were proposed [5]. The mechanism of their action on changing the properties of AUC was not discussed. Recent studies have shown that it depends on the degree of acidity and aggregation of the absorbing complex [6-7]. Therefore, on soil samples of different degrees of

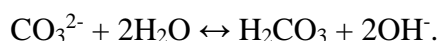
acidity and aggregation (tab. 2), in columns with separated layers, the interaction of ameliorants with AUC was studied at infiltration of 0.5 annual precipitation norm and higher.

Table 2 – Physicochemical characteristics of samples of illuvial horizons of sod-podzolic soils used for model studies (Vladimir Oblast)

№ of cut	Layer depth, cm	Humus, %	S	H <sub>H</sub>	H <sub>ex</sub>	Al <sub>ex</sub> , mg/100 g soil	pH <sub>CS1</sub>	Particle content, %	
			meq/100 g of soil					<0.001 mm	<0.01 mm
1, Pechuga	45-57	0.34	6.90	9.10	4.16	35.4	3.66	25.4	38.4
2, Shepelevo	54-66	0.27	6.90	3.14	1.10	2.50	4.04	13.3	22.7

Notes: S – sum of absorbed bases; H<sub>H</sub> – hydrolytic acidity; H<sub>EX</sub> – exchange acidity.

On very strongly acidic and strongly acidic weakly aggregated soils (tab. 3), a decrease in acidity occurs due to hydroxyl ions (OH<sup>-</sup>), formed by the interaction of CO<sub>3</sub><sup>2-</sup> ions with water. The latter are one of the products of CaCO<sub>3</sub> (lime) dissolution in water, that is, the formation of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> ions. The interaction of CO<sub>3</sub><sup>2-</sup> with water in this case proceeds mainly according to the reaction:



The resulting OH<sup>-</sup> ions bind hydrogen ions to slightly dissociated (H<sub>2</sub>O) and aluminum ions to form slightly soluble (Al(OH)<sub>3</sub>) compounds. The places of bound H<sup>+</sup> and Al<sup>3+</sup> ions are occupied by C ions Ca<sup>2+</sup> (Mg<sup>2+</sup>).

Thus, the utilization rate of dolomite flour (DF) in the columns, introduced in half and full doses of hydrolytic acidity, varied from 0.93 to 0.81 for its decrease (tab. 3), and gypsum was 0.183.

Table 3 - Completeness of interaction of ameliorants with AUC of sod-podzolic soil

Option	Column layer, cm	pH <sub>WAT</sub> , soil: water 1:0.5	V, %	Undissolved carbonates, meq / 100 g of soil	Ameliorant utilization rate, %
Control	0-10	4.70	43.9	Did not contribute	-
	10-20	4.68	45.4		
	20-30	4.58	42.9		
	30-40	4.46	41.9		
Gypsum in a layer of 0-20 cm at 1.05 H <sub>H</sub>	0-10	4.72	50.5	Did not contribute	18.3
	10-20	4.34	45.8		
	20-30	4.33	44.6		
	30-40	4.37	44.1		
DF in a layer	0-10	5.20	72.4	None	

of 0-20 cm at 0.52 H <sub>H</sub>	10-20	5.38	72.2	>>	93.2
	20-30	4.78	45.0	Did not contribute	
	30-40	4.62	43.0		
DF in layer 0- 20 cm at 1.05 H <sub>H</sub>	0-10	6.11	88.1	None	80.8
	10-20	6.21	89.3	>>	
	20-24	-	61.9	Did not contribute	
	24-30	-	46.1		
	30-40	4.56	43.4		

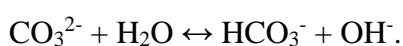
Even at a higher (by an order of magnitude) concentration of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions (tab. 4) in the filtrates (liquid phase), the decrease in hydrolytic acidity in the case of gypsum is lower than that with dolomite flour, as evidenced by the utilization rates of ameliorants.

Table 4 - Concentration of the sum of Ca<sup>2+</sup> and Mg<sup>2+</sup> cations in portions of the filtrate, mg-eq/l

Test variant	№ of portion							Average
	1	2	3	4	5	6	7	
Control	1.25	0.91	0.96	1.20	0.81	0.95	1.33	1.05
0,52 H <sub>H</sub> DF	1.83	0.73	1.40	1.02	0.72	0.72	0.72	1.13
1,05 H <sub>H</sub> DF	2.18	1.40	1.20	1.46	1.61	0.92	1.36	1.46
1,05 H <sub>H</sub> of gypsum	18.4	53.8	63.6	51.7	-	-	-	50.0
0,52 H <sub>H</sub> DF + 0,52 H <sub>H</sub> of gypsum	19.3	49.8	30.8	38.6	-	-	-	36.4

At a maximum concentration of bivalent cations of 2.18 mg-eq/l on strongly acidic soils, OH<sup>-</sup> ions interacted with absorbed H<sup>+</sup> and Al<sup>3+</sup> ions, most of which were located mainly on the outer surface of the absorbing soil complex. This follows from the results of work [8]), in which a more intense destruction of the soil structure with an increase in soil acidity was observed. Equilibrium pH values in the liquid phase were set in the range of 5.1-6.2. The reclamation effect of the lime-containing ameliorant is established mainly in the layer of its introduction. On very strongly acidic soils, the combination of dolomite flour (DF) and gypsum compared to DF did not contribute to a further increase in the DF utilization factor.

On strongly, medium and weakly acidic, *more aggregated soils*, the main agent for neutralizing soil acidity - carbonate ions - interacted with water according to the reaction:



In this case, the hydroxyl ions interacted mainly with the surface located hydrogen and aluminum ions, and the hydrolysis of  $\text{CO}_3^{2-}$  proceeded through the first stage. The concentration of divalent cations  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the liquid phase (up to 4 mg-eq/l) was insufficient for reaggregation of the AUC and displacement of intra-aggregate ions of hydrogen and aluminum. The equilibrium values of  $\text{pH}_{\text{WAT}}$  (1:0.5) of the samples after the interaction of the ameliorant with the soil were about 6.0 when using a dose equivalent to 0.66 of the hydrolytic acidity, and 1.31  $\text{H}_\text{H}$  - about 6.4 and higher. The coefficient of use of the dissolved ameliorant to reduce  $\text{H}_\text{H}$  was 0.5-0.6. In this case, the reclamation effect of the DF dose (0.66  $\text{H}_\text{H}$ ) was observed in the application layer (0-20 cm), and its 1.31  $\text{H}_\text{H}$  dose was also observed in the deeper layer of 20-30 cm (tab. 5).

Table 5 - Influence of doses of dolomite flour on the physicochemical properties of different layers of columns of horizon  $\text{B}_1$  of sod-podzolic soil of light loamy granulometric composition

Layer depth, cm	$\text{H}_\text{H}$	S	$\text{H}_\text{H} + \text{S}$	$\text{H}_\text{EX}$	T, %	$\text{Al}_{\text{ex}}$ , mg/100 g	$\text{pH}_{\text{WAT}}$ 1:0,5
	meq/100 g of soil						
1. Control							
0-10	2,82	6,4	9,22	0,66	69,4	2,25	5,60
10-20	3,50	5,8	9,30	0,82	62,4	3,00	5,09
20-30	2,97	6,6	9,57	0,62	69,0	2,50	5,46
30-40	2,80	6,4	9,20	0,60	69,6	2,52	5,47
2. 2.06 mEq of DF per 100 g of soil in 2 layers (0.66 $\text{H}_\text{H}$ , 7.21 mEq/column)							
0-10	2,10	8,8	10,9	0,08	80,7	0,45	6,10
10-20	1,92	8,2	10,1	0,05	81,0	0,25	5,95
20-30	3,32	6,2	9,52	0,75	65,1	1,89	5,26
30-40	3,50	6,0	9,50	0,77	63,2	2,79	4,99
3. 4.12 mEq of DF per 100 g of soil in 2 layers (1.31 $\text{H}_\text{H}$ , 14.42 mEq/column)							
0-10	1,75	9,0	10,75	0,04	83,7	0,18	6,36
10-20	1,57	8,8	10,37	0,02	84,9	None	6,55
20-30	1,92	7,5	9,42	0,20	79,6	0,63	6,07
30-40	2,80	6,4	9,20	0,57	69,6	2,16	5,51

On soils of light loamy granulometric composition, the combination of lower doses of dolomite flour and gypsum, applied in 2 layers of  $2/3 \text{H}_\text{H}$  each, compared with dolomite flour alone, also led to a further decrease in  $\text{H}_\text{H}$  and exchangeable acidity, exchangeable aluminum in layers deeper than the applied layer (20-40 cm), a slight increase in  $\text{pH}_{\text{WAT}}$  (tab 6). The latter did not contradict the

growth of absorbed bases from 6.0-6.2 to 6.55-7.10 meq/100 g of soil. This was also observed with a combination of a dose of DF 2/3 of hydrolytic acidity and gypsum 1/3 H<sub>H</sub>.

Under the influence of a gypsum dose of 1.31 H<sup>H</sup> in the upper soil layer of 0-20 cm, a decrease in hydrolytic acidity was not established, but in the 20-40 cm layer it increased. In comparison with the control column without the ameliorant (tab. 5), the decrease in pH was 0.5 units. However, in the 0-20 cm layer, the amount of exchangeable bases increased, in the 0-30 cm layer, exchangeable acidity decreased. This indicates that a high concentration of calcium ions displaces hydrogen ions of a different nature (intra-aggregate) from the PPC.

Table 6 - Influence of doses of dolomite flour and gypsum on the physicochemical properties of different layers of the columns of horizon B<sub>1</sub> of sod-podzolic soil of light loamy granulometric composition

Layer depth, cm	H <sub>H</sub>	S	H <sub>H</sub> + S	H <sub>EX</sub>	T, %	A <sub>lex</sub> , mg/100 g	pH <sub>WAT</sub> 1:0,5
	meq/100 g of soil						
4.12 mEq of gypsum per 100 g of soil in 2 layers (1.31 H <sub>H</sub> , 14.42 mEq/column)							
0-10	3,06	7,00	10,1	0,28	69,3	3,06	5,15
10-20	2,71	6,80	9,51	0,32	71,5	3,42	4,97
20-30	3,59	6,30	9,89	0,38	63,7	3,69	4,91
30-40	3,73	6,50	10,2	0,59	63,7	2,97	5,00
2.06 mEq/100 g of soil DF and gypsum in 2 layers (7.21 mEq/column)							
0-10	1,92	8,68	10,6	0,06	81,9	0,50	5,52
10-20	1,75	8,38	10,1	0,03	82,7	0,45	5,77
20-30	2,30	7,10	9,40	0,37	75,5	1,53	5,45
30-40	2,70	6,55	9,25	0,51	70,8	2,43	5,16
2.06 mEq of DF and 1.03 mEq of gypsum per 100 g of soil in 2 layers (7.21 + 3.60 mEq)							
0-10	1,92	8,70	10,6	0,17	82,1	0,27	6,08
10-20	1,84	7,60	9,44	0,12	80,5	0,20	6,12
20-30	2,71	6,80	9,51	0,55	71,5	2,52	5,34
30-40	2,94	6,75	9,69	0,67	69,7	2,98	5,24

This is confirmed by the author's research on the mechanism of coagulation of sol isolated from the eluvial horizon of the solonetz by cations of various valences (figure). It can be seen that its coagulation is associated with the interaction of the studied cations with different numbers of functional groups of the sol, which leads to a complete or partial loss of its charge. With an increase in the concentration of K<sup>+</sup> and H<sup>+</sup> ions, the charge of 3 functional groups is neutralized, and the

concentration of aluminum ions - one, calcium ions - one or more. Obviously, the coagulation of the sol by divalent and trivalent cations occurs due to the strong binding of certain functional groups of the sol by them.

And in the case of interaction of gypsum with the absorbing complex of soddy-podzolic soil (tab. 6), at a high concentration of  $\text{Ca}^{2+}$  ions in the liquid phase, their strong bond with certain places of the AUC (acidic functional groups) occurs, which leads to the displacement of hydrogen ions into the liquid phase, the degree of saturation with bases, reaggregation of AUC and subsequent coagulation of soil colloids. In the case of the combined use of dolomite flour and gypsum, these displaced hydrogen ions are bound by hydroxyl ions formed during the hydrolysis of  $\text{CO}_3^{2-}$  not only at the 1st, but also at the 2nd stage. This makes it possible to increase the utilization rate of dolomite flour (lime-containing ameliorant) to reduce the hydrolytic acidity not only in the layer of DF and gypsum application, but also deeper than it (tab. 7).

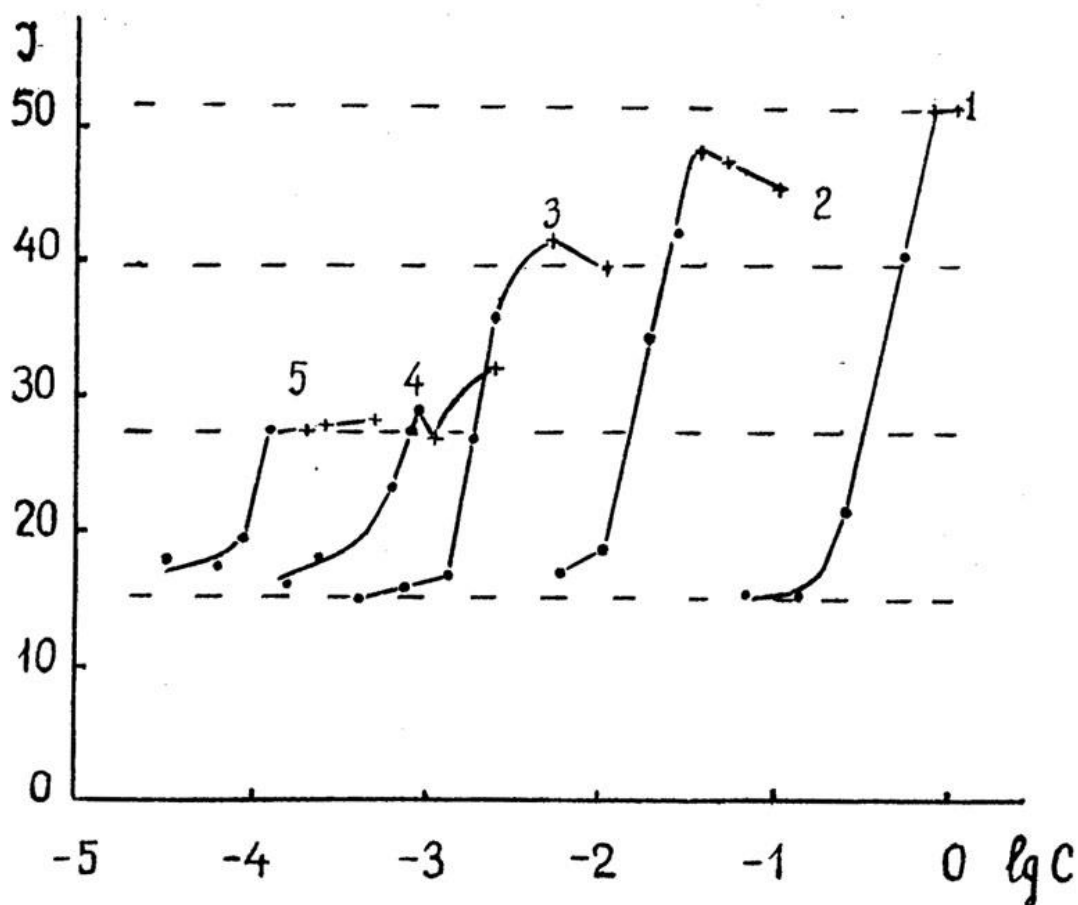


Figure - Change in the intensity of light scattering by the sol isolated from the eluvial horizon of the solonetz versus the logarithm of the ion concentration (g-ion/l)[9]:

1 -  $\text{K}^+$ , 2 -  $\text{H}^+$ , 3 -  $\text{Mg}^{2+}$ , 4 -  $\text{Ca}^{2+}$ , 5 -  $\text{Al}^{3+}$ .

+ - designations corresponding to visually observed coagulation of the sol.

When dolomite flour was used in doses of 0.66 and 1.31  $\text{H}_\text{H}$ , the coefficient of its use to reduce hydrolytic acidity in the 0-20 cm layer was 0.56 and 0.36, respectively, and for the entire 0-40 cm

soil layer - 0.30 and 0.49, the degree of hydrolysis of  $\text{CO}_3^{2-}$  - 55.7 and 54.0% (tab. 7). In this case, hydrolysis at the 1st stage ( $\text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{OH}^-$ ) proceeded completely (100%), and at the 2nd ( $\text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 + \text{OH}^-$ ) – by 11.4 and 8.0%. The degree of hydrolysis of carbonate ions was determined by the  $\text{pH}_{\text{WAT}}$  of the soil (1:0.5) in soil layers of 0-10 and 10-20 cm columns after interaction with ameliorants.

Table 7 - Efficiency of using dolomite flour and its mixtures with gypsum

Option (№ of column)	Column layer, cm	$H_H$ , meq/100 g of soil	Coefficient of use of dolomite flour in the soil layer 0-20 cm/degree of hydrolysis $\text{CO}_3^{2-}$	Total utilization rate of dolomite flour/degree of hydrolysis $\text{CO}_3^{2-}$
2. 2.06 mEq of dolomite flour per 100 g of soil in 2 layers (7.21 mEq/column)	0-10	2,10	<b>0.56/55.7</b>	0.30/55.7
	10-20	1,92		
	20-30	3,32		
	30-40	3,50		
3. 4.12 mEq of dolomite flour per 100 g of soil in 2 layers (14.42 mEq/column)	0-10	1,75	0.36/54.0	<b>0.49/54.0</b>
	10-20	1,57		
	20-30	1,92		
	30-40	2,80		
4. 2.06 mEq/100 g of soil of dolomite flour and gypsum in 2 layers (7.21 mEq)	0-10	1,92	0.64/82.8	<b>0.83/82.8</b>
	10-20	1,75		
	20-30	2,30		
	30-40	2,70		
5. 4.12 mEq of gypsum per 100 g of soil in 2 layers (14.42 mEq/column)	0-10	3,06	0.07*	Increase in $H_H$ by 8.3 %
	10-20	2,71		
	20-30	3,59		
	30-40	3,73		
6. USD 2.06 mEq. flour and 1.06 mEq of gypsum per 100 g of soil per layer (7.21 + 3.71 mEq)	0-10	1,92	0.62/74.2	<b>0.65/74.2</b>
	10-20	1,84		
	20-30	2,71		
	30-40	2,94		
* - gypsum utilization rate				



Adding the same dose of gypsum to DF ( $2/3 H_H$ ) increased the utilization factor of DF in the 0-20 cm layer from 0.56 to 0.64, and in the 0-40 cm layer - to 0.83. In the latter case, this is due to a significant decrease in  $H_H$  and deeper than the layer of ameliorants. Adding gypsum to the same dose of DF at a dose of  $1/3 H_H$  led to an increase in the utilization rate of the former in the 0-20 cm layer to 0.62, and in the 0-40 cm layer - to 0.65. With the combined use of DF and gypsum, the reclamation effect increased with an increase in the dose of gypsum. When only gypsum was applied at a dose of  $1.31 H_H$ , only 7% of this ameliorant was used to reduce  $H_H$  in the 0-20 cm layer, and even its increase by 8.3% was observed in the entire 0-40 cm layer.

On gray forest soils of the Upper Volga region, with infiltration through the column of 0.5 and total annual precipitation rates and an increase in the DF dose from single to double (in  $H_H$ ), the utilization coefficient of dissolved DF increased from 65.4 to 75.7%, and with a combination of single and double doses of DF with gypsum ( $0.5 H_H$  each) - from 79.6 to 108%, respectively.

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