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## Absorption Capacity and Composition of Exchange Cations in Different Types of Coal

T. V. NECHAEVA, D. A. SOKOLOV

*Institute of Soil Science and Agrochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia**E-mail: nechaeva@issa-siberia.ru*

### Abstract

The absorption capacity of different types of coal from the largest deposits of West Siberia (Kansk-Achinsk, Kuznetsk and Gorlovskiy basins), composition and content of biogenic elements in the form of cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ) in water-soluble and exchange forms are studied. It is shown that the absorption capacity of coal, as measured by cation exchange capacity, increases with an increase in the coal metamorphism degree in the sequence: anthracite  $\rightarrow$  coal  $\rightarrow$  brown coal, and with an increase in dispersity of carbon particles from coarse size fractions to smaller ones. The major exchange positions in coal are occupied mainly by calcium, which, in turn, negatively affects the ability of coal to participate in the exchange processes with other biogenic elements. The ability of coal to absorb cations from solutions is largely determined not by the geologically caused density and porosity of coal but mainly by the total surface area of particles. The values of the cation exchange capacity of coal are comparable with the values for the most fertile soils of West Siberia (agrochernozems) and their parent rocks (loess-like loam) or even exceed them.

**Keywords:** anthracite, coal, brown coal, cation exchange capacity, potassium, calcium, magnesium, sodium

### INTRODUCTION

It is known that the value of different kinds of coal is determined not only by energy-related properties but also by the possibility to extract some rare elements and numerous products of technological processing (carbonaceous materials, humic preparations, etc.) [1, 2]. Special value is rendered to coal by their absorption capacity, which is exhibited not only in the neutralization of a number of toxic elements and compounds by coal but also in the possibility to form a depot of biogenic elements under the conditions of technogenic landscapes [3–5]. The ability of coal to participate in the process of cation exchange in the forming young soils has a positive effect on the rate of recovery of technogenically disturbed territories. However, the potential of ecological functions of coal often remains unimplemented.

The goal of the work was to evaluate the capacity of different kinds of coal to absorb biogenic elements in water-soluble and exchangeable forms and to reveal the reasons limiting this capacity. This work is a continuation of our studies into the absorption capacity of coal by evaluating its potassium-fixing capacity [6], because potassium is one of the most important biogenic elements, and its compounds are most often used to obtain humic preparations from coal.

### EXPERIMENTAL

The samples of three kinds of coal from the largest deposits of Siberia were chosen as the objects of investigation. These kinds of coal differ from each other in the degree of metamorphization: brown coal from the Nazarovskoe deposit in

the Kansk-Achinsk basin (55°58'N, 90°23'E), black coal from the Listvyanskoe deposit of the Kuznetsk basin (53°39'N, 86°53'E), anthracite from the Gorlovskoe deposit of the Kansk-Achinsk basin (54°34'N, 83°35'E). To carry out a comparative evaluation of the potassium-fixing capacity of coal, we chose the samples of loess-like carbonate loamy soil (below referred to as loam) as the prevailing soil-forming rock at the territory under consideration, and the humus horizon of agricultural black soil (chernozem) as one of the most widespread and economically valuable types of soil in Siberia. Below all the samples under investigation will be designated using a common term – substrates.

Evaluation of the absorbing capacity of coal was carried out in two versions. In the first version, the cation-exchange capacity (CEC) was considered for three kinds of coal over granulometric fractions. In the second version, a laboratory experiment aimed at the determination of the potassium-fixing capacity of all substrates presented above was carried out. Substrate preparation for experiments included bringing them to air-dry state and sieving through a sieve with 1 mm mesh. The evaluate CEC of three kinds of coal over granulometric fractions, the samples were additionally sieved through the sieves with 0.5, 0.25 and 0.1 mm mesh. The CEC of the substrates was determined using the Bobko-Askinasi method in CINAO modification [7]. It is generally accepted that the amount of hydrogen ions able to be substituted by metal cations corresponds to the amount of carboxyl groups in the sample under investigation [8]. However, recently some works appeared in which evidence for the participation of hydrogen atoms of hydroxyl groups in cation exchange processes was reported [9, 10].

The potassium-fixing capacity of the substrates was considered under the conditions of laboratory experiments for 150 days. Potassium chloride KCl (Kh. Ch. reagent grade) was used as potassium-containing fertilizer; the slat was added once in the form of the aqueous solution in doses 25 and 50 mg of K per 100 g of the substrate (versions  $K_{25}$  and  $K_{50}$ , respectively). In parallel, an experiment without the addition of fertilizers ( $K_0$  version) was carried out. For the more complete manifestation of the capacity of substrates to fix potassium, the experiment was carried out in the mode of alternating wetting and drying with sampling after 1, 5, 15, 30 and 150 days. The experiment was carried out twice. The sample number ( $n$ ) for each substrate with three

versions of the experiment and five samplings was  $n = 30$  ( $2 \times 3 \times 5$ ). Potassium initially added into the substrate in the form of the aqueous solution of potassium fertilizers and then transformed into the form not amenable for extraction with a 1 M  $\text{CH}_3\text{COONH}_4$  solution was considered as fixed. Potassium fixation was calculated with respect to the  $K_0$  version in percent of the dose introduced. A more detailed description of the arrangement of laboratory experiments and results on the evaluation of the potassium-fixing capacity of coal were presented in [6].

The content of potassium, calcium, magnesium and sodium in the substrates was determined by means of atomic absorption spectrometry with the help of AAnalyst 400 analyzer (Perkin Elmer Inc., USA). Two forms of elements were considered: water-soluble (at the ratio of substrate/ $\text{H}_2\text{O}$  (distilled grade) = 1 : 5) and exchangeable (at the ratio of substrate/extractant (1 M  $\text{CH}_3\text{COONH}_4$  of Kh. Ch. reagent grade, pH 7.0) = 1 : 10). Calculation of the exchangeable form of the elements was carried out using the difference method taking into account subtraction of their water-soluble form, because a stronger extractant extracts an element that passes into weaker extracts. The results are presented as the contents of cations  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  in absolutely dry substrates. To compare the relations between cations in substrates, the total cation content was conventionally accepted to be 100 %.

Statistical treatment of the experimental data was carried out using the Microsoft Office Excel 2007 and SNEDECOR V. 5.80 software [11].

## RESULTS AND DISCUSSION

### *Substrate characterization with respect to CEC, composition and cation content*

Results of investigations showed that CEC for different kinds of coal varies depending on the degree of coal metamorphization (Table 1). One can see that with respect to CEC value brown coal possesses the highest absorption capacity, which may be typical only for separate components of soil mass (humic substances, smectite minerals, etc.). Anthracite and black coal have lower CEC values than brown coal; loam and black soil have a medium absorption capacity which is characteristic of soil with not very high humus content.

It is important to stress that the differences in CEC values of coal kinds are determined not only by the degree of coal metamorphization but also

TABLE 1

Initial properties of substrates before the experiments of potassium fixation

Substrate	CEC, cmol(equiv)/kg	Cation content (water-soluble/exchangeable forms), cmol(equiv)/kg			
		K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
Anthracite	10	0.03 / 0.02	0.11 / 0.005	0.52 / 2.58	0.10 / 0.58
Black coal	18	0.11 / 0.08	0.41 / 0.56	0.27 / 5.14	0.12 / 1.49
Brown coal	106	0.03 / 0.04	0.17 / 0.09	3.60 / 46.29	1.34 / 13.96
Loam	30	0.04 / 0.49	0.14 / 0.04	0.42 / 30.74	0.07 / 2.67
Agricultural black soil	40	0.04 / 0.53	0.12 / 0.09	0.26 / 17.45	0.09 / 3.34

Note. 1. CEC is the cation exchange capacity. 2. Cation content is represented in two forms: water-soluble/exchangeable.

by the dispersity of coaly particles (Fig. 1). For instance, CEC of the sandy fractions of coal increases inversely proportional to a decrease in their size (Spearman correlation coefficient for different kinds of coal varied from  $-0.69$  to  $-0.99$  for  $n = 12$  for each kind): the minimal values are

characteristic of the functions of coarse sand (0.5–1 mm). The CEC values for this fraction in all coal kinds are 2 times lower than the CEC of coarse dust (less than 0.1 mm). The values obtained for CEC of the fractions of different kinds of coal provide evidence that the capacity of coal

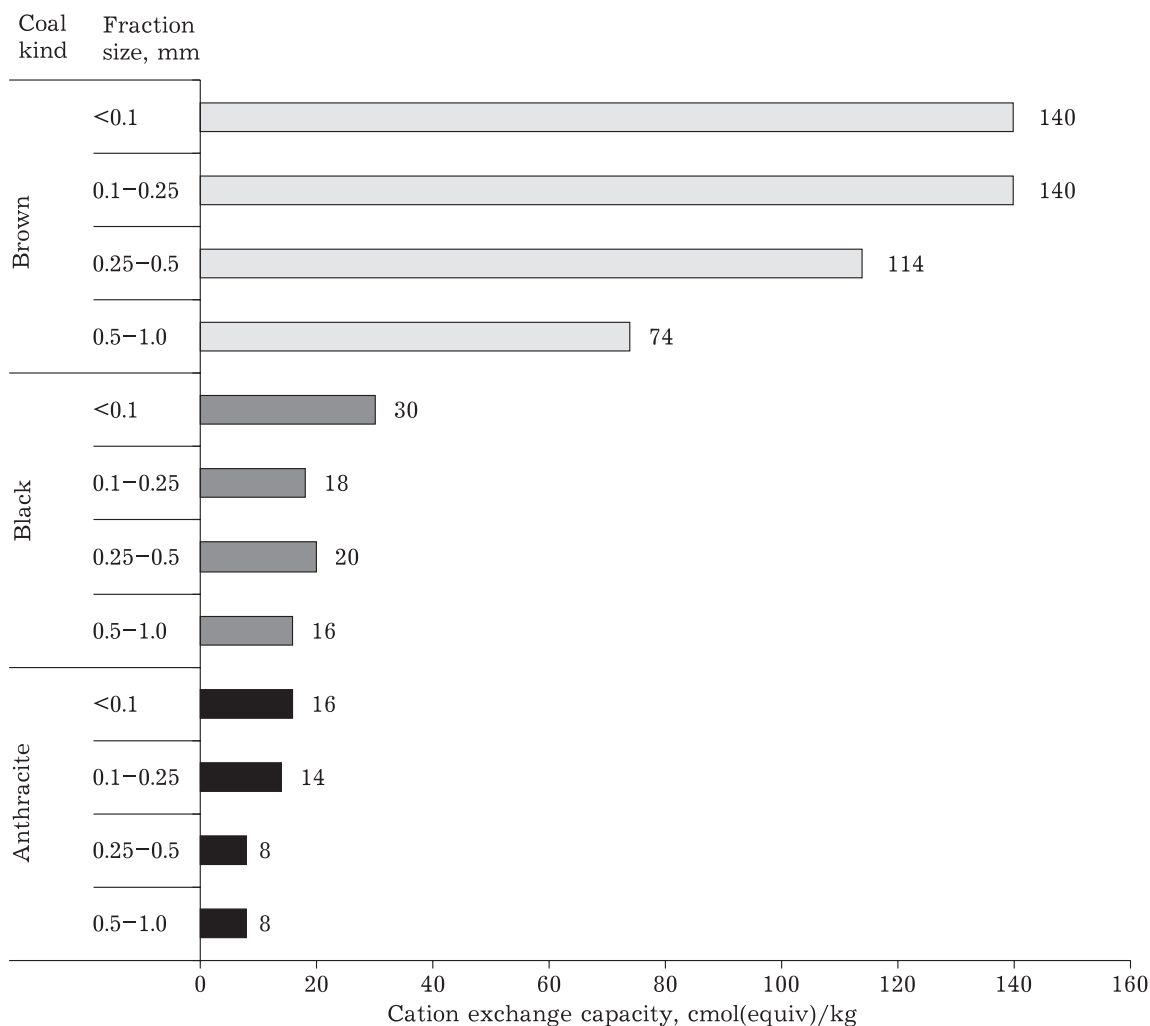


Fig. 1. Differentiation of the values of cation exchange capacity (CEC) for different kinds of coal over granulometric fractions.

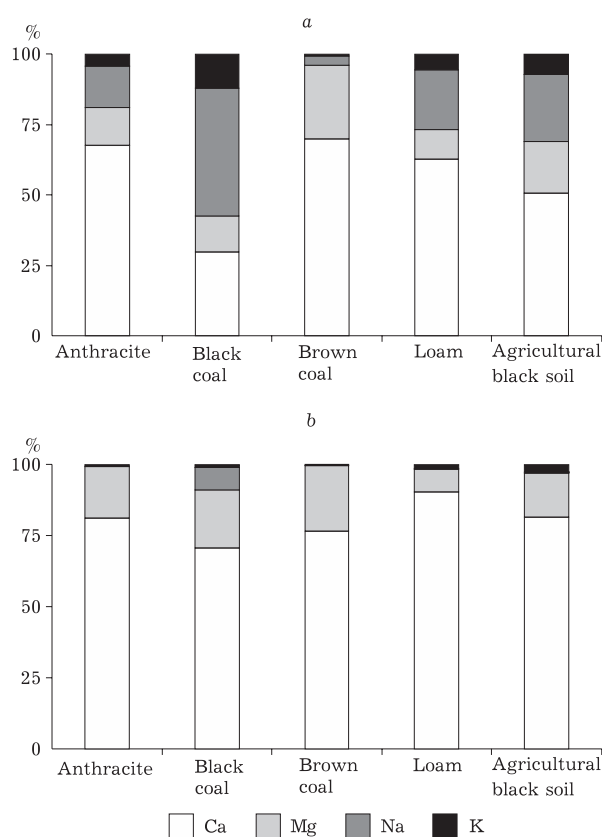


Fig. 2. Ratio of cations in substrates before the experiment on potassium fixation: water-soluble (a) and exchangeable (b) forms.

to absorb cations from solutions is determined by the geologically conditioned density and porosity, and by the total surface area of the particles.

The differences between the substrates in the content of biogenic elements in the form of cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) in water-soluble and exchangeable forms were established (see Table 1). A comparison between the ratio of cations in the water-soluble form showed (Fig. 2, a) that in brown coal a substantial fraction is first of all due to calcium (70 %) and magnesium (26 %). In black coal, sodium and calcium dominate (45 and 30 %, respectively), at the same time, magnesium and potassium are present (13 and 12 %, respectively). With respect to the cation ratio, anthracite is closer to black soil and loam; calcium accounts for more than a half (51 to 68 %), while other cations form the descending sequence: sodium (15–24 %) → magnesium (10–18 %) → potassium (4–7 %).

Comparing the cation ratios in the exchangeable form, one can see (see Fig. 2, b) that substantial fractions in all substrates are occupied first of all by calcium and then magnesium: in coal 71–81 and 18–23 %, in black soil 82 and 16 %, in loam 91 and 8 %, respectively. The fraction of sodium in coal varies substantially – 0.1–8 %, while the fraction of potassium remains the lowest – from 0.1 to 1.1 %. In black soil and loam, the fraction of potassium was 2.5 and 1.5 %, respectively, which is higher than the fraction of sodium – 0.4 and 0.1 %, respectively.

So, the data obtained on CEC provide evidence of different capacities of different kinds of coal to participate in exchange processes in young soils being formed in technogenic landscapes. Initially, before the laboratory experiment on potassium

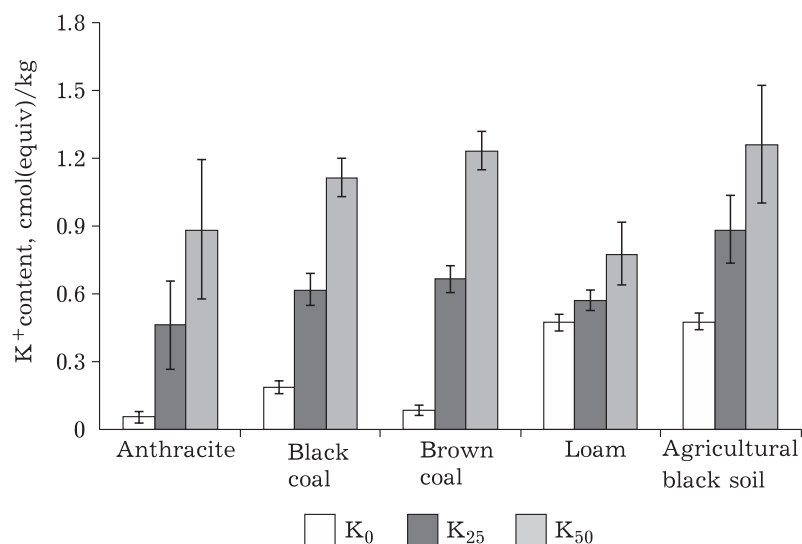


Fig. 3. Content of exchange potassium (including water-soluble form) after the introduction of fertilizers in doses 0, 25 and 50 mg K per 100 g of substrate ( $K_0$ ,  $K_{25}$  and  $K_{50}$  versions, respectively) as average during the time of experiment (150 days). Vertical bars mean standard deviations (s) from arithmetic mean values (M) in the form of columns ( $M \pm s$ ).

fixation, calcium was prevailing among the considered biogenic elements in the substrates, both in water-soluble and in exchangeable forms. Black coal was an exception because sodium was prevailing in the water-soluble form.

#### *Absorption capacity of substrates for potassium fixation as example*

As average, within 150 days, the introduction of potassium fertilizers caused a substantial increase in the sum of water-soluble and exchangeable potassium proportionally to the dose (Fig. 3), especially in anthracite (by a factor of 9 and 16 in versions  $K_{25}$  and  $K_{50}$ , respectively, with respect to  $K_0$ ) and in brown coal (8 and 14 times, respectively), these kinds being characterized by the lowest potassium content. The substrates are arranged as the following sequence with respect to potassium-fixing capacity (%): loam (80) → black soil (38) → anthracite (36) → black coal (30) → brown coal (10) [6]. So, among substrates, the lowest potassium-fixing capacity was demonstrated by brown coal, while the highest one was demonstrated by loam, which is connected with the presence of clay minerals possessing the high capacity to fix potassium [12]. Potassium fixation in black coal and in anthracite is substantially

higher than in brown coal, at the same time the values of this parameter are rather close to black soil. The same regularities were obtained by us previously on the basis of the results of the first 30 days of the experiment [13].

Consideration of the content of biogenic elements as cations ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) in the exchangeable and water-soluble forms after 150 days from the introduction of fertilizers revealed small changes in the content of the water-soluble form (Table 2). Comparing the concentrations of cations in water-soluble form (Fig. 4, a) one can see that in anthracite, with an increase in the fraction of potassium from 1.5 % in version  $K_0$  to 48 % in version  $K_{50}$ , the fraction of calcium decreased sharply (from 89 to 37 %), in black coal, with an increase in the fraction of potassium in fertilized versions, the fractions of sodium and calcium decreased through initially they were prevailing among cations. In brown coal, with its initially highest absorption capacity, with an increase in the fraction of water-soluble potassium from 0.7 % in version  $K_0$  to 9.6 % in version  $K_{50}$ , the fractions of the other three cations remained in approximately the same relations.

Comparison between cation contents in the exchangeable form revealed (see Fig. 4, b) that

TABLE 2

Cation content 150 days later after the introduction of potassium fertilizers into the substrates

Substrate	Version	Water-soluble/exchangeable forms, cmol(equiv)/kg			
		$K^+$	$Na^+$	$Ca^{2+}$	$Mg^{2+}$
Anthracite	$K_0$	0.02 / 0.02	0.05 / 0.05	1.27 / 7.95	0.09 / 0.36
	$K_{25}$	0.19 / 0 <sup>a</sup>	0.05 / 0.02	0.86 / 13.70	0.08 / 0.23
	$K_{50}$	0.32 / 0 <sup>a</sup>	0.05 / 0.02	0.25 / 10.93	0.05 / 0.25
Black coal	$K_0$	0.08 / 0.09	0.43 / 0.07	0.52 / 9.80	1.39 / 10.72
	$K_{25}$	0.20 / 0.35	0.40 / 0.34	0.51 / 10.61	1.47 / 11.12
	$K_{50}$	0.43 / 0.64	0.42 / 0.34	0.63 / 11.57	1.69 / 9.36
Brown coal	$K_0$	0.03 / 0.04	0.18 / 0.06	2.37 / 56.43	1.39 / 10.72
	$K_{25}$	0.25 / 0.34	0.22 / 0.08	3.03 / 57.78	1.47 / 11.12
	$K_{50}$	0.56 / 0.70	0.25 / 0.05	3.33 / 57.63	1.69 / 9.36
Loam	$K_0$	0.02 / 0.47	0.09 / 0.09	0.51 / 38.77	0.07 / 2.12
	$K_{25}$	0.02 / 0.50	0.06 / 0.10	0.64 / 42.45	0.08 / 2.17
	$K_{50}$	0.04 / 0.55	0.09 / 0.08	1.14 / 44.36	0.13 / 2.22
Agricultural black soil	$K_0$	0.03 / 0.45	0.05 / 0.04	0.45 / 22.99	0.13 / 3.00
	$K_{25}$	0.05 / 0.57	0.05 / 0.05	0.89 / 23.16	0.20 / 2.56
	$K_{50}$	0.08 / 0.74	0.07 / 0.05	0.95 / 27.20	0.23 / 2.74

Note. Versions  $K_0$ ,  $K_{25}$  and  $K_{50}$  correspond to single introduction of fertilizers in doses 0, 25 and 50 mg K per 100 g of substrate.

<sup>a</sup> K detected is completely represented by the water-soluble form of the element.

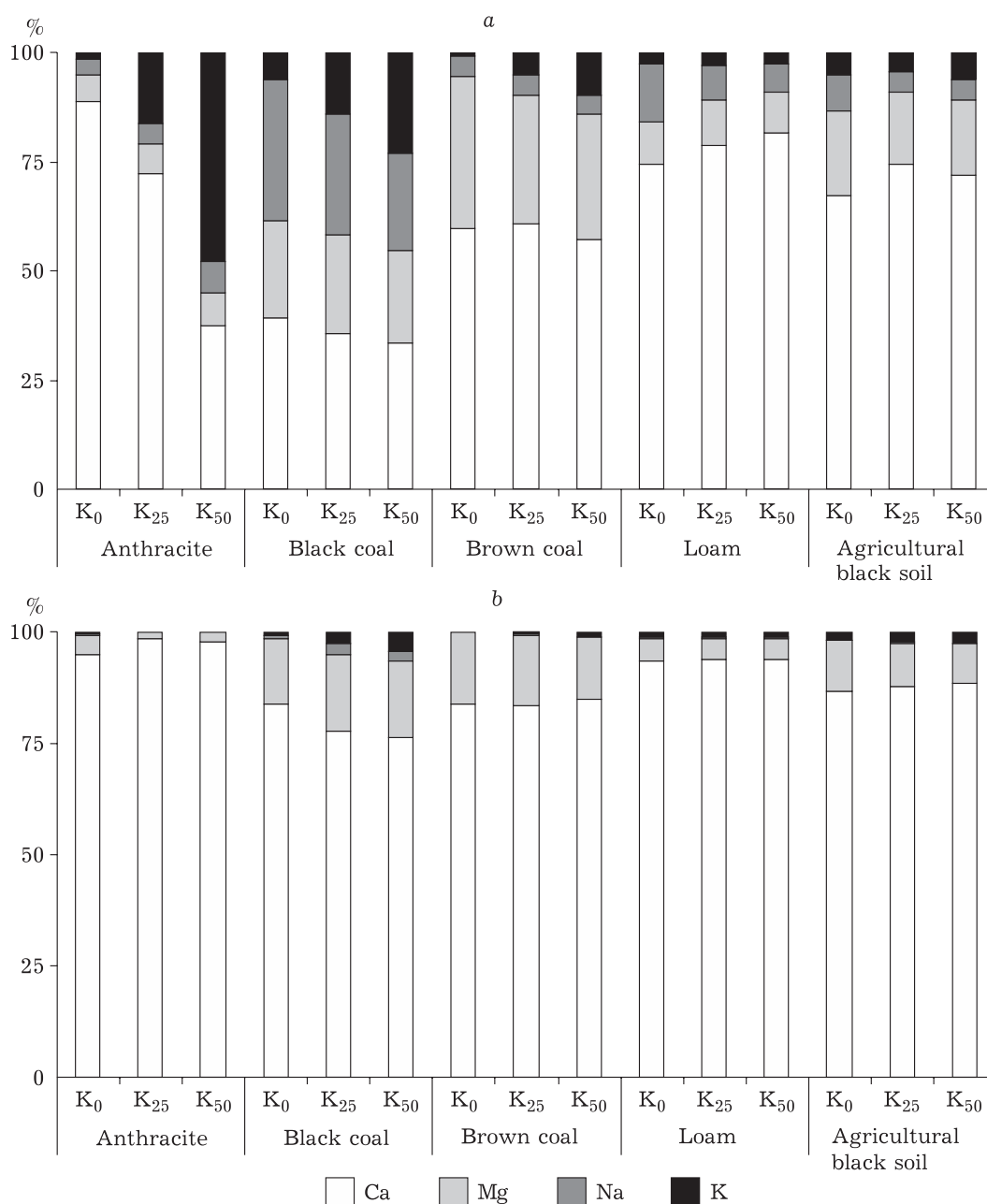


Fig. 4. Ratios of cations after 150 days from the introduction of potassium fertilizers into substrates: water-soluble (a) and exchangeable (b) forms.

after 150 days of the experiment calcium was dominating in all substrates and versions: its content was within the range 76 to 98 %. Therefore, the major exchangeable positions in the substrates under consideration are occupied mainly by calcium. With respect to the ratio of calcium to magnesium, black coal and brown coal were closer to black soil, while anthracite was closer to loam. The fractions of potassium and sodium remained insignificant in comparison with calcium and magnesium in all substrates.

In general, coal kinds at higher metamorphization degree (black coal and anthracite) are as good as zonal soils of West Siberia in potassium-fixing capacity [14, 15] and, possessing absorption capacity, they affect the functioning of young soils in technogenic landscapes because fine coal particles account for 7 % and more of fine grained soil [16, 17]. Black coal and anthracite get into dumps together with macrofragmental rocks possessing insignificant absorption capacity. Brown coal is brought to dumps together with loamy and

clay rocks [17], which minimizes its participation in the processes taking part in young soils of technogenic landscapes.

## CONCLUSION

Thus, investigations allow us to conclude that the absorption capacity of different kinds of coal is determined not only by the degree of coal metamorphization but also by particle size. The absorption capacity of coal evaluated on the basis of CEC increases as a sequence: anthracite → black coal → brown coal, in the granulometric aspect it increases from coarse fractions to finer ones. The CEC values of coal are comparable with those for the most fertile soils of Siberia (agricultural black soil) and in their soil-forming rocks (loess-like loam) or even exceed them. However, the potential of the absorption capacity of coal in exchange processes is implemented only partially because the major exchange positions are occupied mainly by calcium. Calcium in the exchangeable form is reliably held by coal because the fraction of calcium does not decrease within 150 days after substrate saturation with potassium.

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