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The Content of the Forms of Calcium and Sulphur in the Spoil Tip of Initial Soil in the Sulphur Mine "Machów" after Many Years of Its Agricultural and Forestry Land Use

1. Introduction

Calcium and sulphur are basic macro-components necessary for all living organisms. At the same time these components have a strong and antagonistic impact on chemical properties of soil, especially its reaction.

Calcium occurs in many rock-forming minerals (calcite, dolomite, gypsum, anorthite, apatite, phosphorites and others); its content in not limed soils ranges from 0.1% to 1.5%, while in the rendzina soils it can exceed 10% [5, 12]. In the opinion of most researchers even in mineral soils, generally poor in this element, there is enough calcium to meet the requirements of the plants; the reason for its adding to soils in the agricultural areas is the necessity of the improvement of its reaction and structure [5, 11, 12].

The overburden grounds of the sulphur ore making the external spoil tip of the "Machów" Mine – the object of the studies – despite their non-selective moulding and piling, are characterized with a high homogeneity. According to the studies carried out during its construction [2], the upper level of the spoil tip consists in 90% of Tertiary (Miocene) formations – the Krakowiec Clays with the inclusion of (among others) hard limestones, marls and marl tiles, which contain a lot of Ca. These grounds have a grain composition of clays or heavy clays of a very high content of the sub-fraction of colloid clay (usually above 40% – Tabs 1, 2), with a high participation of montmorillonite containing cations of calcium in the inter-pack spaces (Ca-montmorillonite). The total content of calcium in the grounds of the spoil tip horizons near the surface, before starting the reclamation works, was on average about 5% [8], which is intermediate between the content in not limed soils and the rendzina soils. The predominant part of calcium occurred in the form of carbonates, the content of which was usually around 10% [2, 8].

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Table 1. Basic properties of the soils in the analysed plots in the forestry managed rubble heap "Machów"

Plot no.	Depth	Fractions [%]		pH	EC*	$CaCO_3$
	[cm]	<0.02 mm	<0.002 mm	1 M KCl	[mS · cm^{-1}]	[%]
1	0–10	56	34	7.29	0.204	14.25
	10–20	67	40	7.46	0.146	17.90
	20–30	74	44	7.56	0.206	14.20
	30–50	73	44	7.37	1.953	19.10
	50–70	81	36	7.41	1.952	14.50
2	0–10	63	37	7.26	0.25	7.20
	10–20	75	46	7.51	0.171	9.35
	20–30	61	43	7.5	0.183	9.20
	30–50	74	44	7.62	0.193	9.80
	50–70	78	43	7.56	1.12	9.10
3	0–10	88	51	7.45	0.21	8.70
	10–20	90	54	7.53	0.26	10.25
	20–30	89	48	7.51	1.01	9.80
	30–50	87	48	7.44	2.02	10.60
	50–70	88	55	7.47	2.00	9.20

* Electrolytic conductivity.

Table 2. Basic properties of the soils in the analysed plots in the agriculturally managed rubble heap "Machów"

Plot no.	Depth	Fractions [%]		pH	EC*	$CaCO_3$
	[cm]	<0.02 mm	<0,002 mm	1 M KCl	[mS · cm^{-1}]	[%]
4	0–10	75	48	7.4	1.16	7.25
	10–20	78	49	7.5	2.05	7.39
	20–30	81	50	7.6	2.04	8.23
	30–50	78	47	7.6	2.20	6.56
	50–70	90	46	7.6	2.25	7.25
5	0–10	65	40	7.5	0.76	5.58
	10–20	69	43	7.5	2.04	5.86
	20–30	65	42	7.5	2.01	4.88
	30–50	68	46	7.6	2.05	4.90
	50–70	66	44	7.6	2.10	5.60
6	0–10	57	36	7.7	1.74	7.28
	10–20	58	25	7.7	2.02	7.28
	20–30	64	42	7.7	2.11	6.72
	30–50	65	44	7.7	2.24	8.82
	50–70	73	48	7.7	3.37	10.08

* Electrolytic conductivity.

Higher content of calcium than in not limed natural soils is also quite often found in the formations of the overburden of lignite mines. In medium and heavy formations of the spoil tips of mines "Bełchatów" and "Adamów" its content reaches 3% [11, 18].

Sulphur in mineral soils comes from three main sources: minerals contained in the bedrock (pyrite, marcasite, gypsum), organic matter and atmospheric pollution [6, 7, 13]. The results of the studies by Motowicka and Terelak [14] indicate that the whole content of this element in mineral soils of Poland usually ranges from 7–107 mg · 100 g^{-1}, and in most cases from 15–20 mg · 100 g^{-1}. Relatively the highest sulphur content is in the rendzina and alluvial soils and soils formed of medium and heavy clays. The total content of sulphur in the grounds of the spoil tip of "Machów", directly after its formation, often exceeded 1%, thus it was about 10 times higher than the upper value of the quoted above range for mineral soils of Poland. In the overburden formations sulphur mainly in the form of sulphides and gypsum and in smaller quantities also as elementary sulphur [1, 2]. The content of this element in the grounds of the spoil tip of lignite mining is usually smaller, except of strongly acidificated Tertiary clays dominating in the overburden of the lignite mine "Turów", which are characterized by a similar content of sulphur as the grounds of the "Machów" spoil tip [3, 11, 17, 18].

The objective of the studies, the results of which are put in this paper, was the analysis of the content of some forms of calcium and sulphur in the grounds of selected plots of the spoil tip of the Open Cast Sulphur Mine "Machów", covered with forest or managed as an agricultural land, after about 30 years from carrying out the reclamation works.

2. Materials and Methods

The studies covered three plots on the top of the spoil tip plateau, reclaimed for the agricultural use and three on the scarp reclaimed as a forest. Reclamation on two plots managed for agricultural purposes and all the forest plots was carried out in 1977–1978. Both plots on the top plateau were in 1978 sown with medick (*Medicago* sp.) and grasses, then in one of them (plot no. 4) in 1981 a strict plot experiment was established to optimize the technology of agriculture, especially the fertilizing of four plants cultivated in the rotation (mangel beet, spring barley, Italian ryegrass, winter wheat). Two rotation cycles were completed and the whole area was sown with medick and grasses and was used as green area [9, 10]. The other plot (no. 5), was used as a meadow practically for the whole period (32 years). On both plots now grass vegetation dominates with the high proportion of weeds and low of the medick. On the other agriculturally used plot (no. 6) remediation measures were taken 6–7 years later, then it was sown with medick and grass and for 20 years has been used as arable land with sowing annual plants every year (mainly the winter wheat and rape).

The plots covered with forest are on the north scarp of a relatively small inclination (15–20%). On each of them different tree species dominates: the pedunculate oak (*Quercus robur*) (plot no. 1), grey alder (*Alnus incana*) (no. 2), European larch (*Larix decidua*) (no. 3).

In autumn 2010 on each of the six plots – three profiles were analysed and the soil samples were taken from five horizons:

a) 0–10 cm,
b) 10–20 cm,
c) 20–30 cm,
d) 30–50 cm,
e) 50–70 cm.

In the randomized soil material (from three individual samples) the following properties were analyzed: granulometric composition – with the Casagrande aerometric method modified by the Prószyński, pH – potentiometric measurement according to PN-ISO 10390:1997, Ca – extracted in the mixture of $HClO_4$ and HNO_3, in water extract with the atomic spectroscopy method, $CaCO_3$ – Scheibler method, the content of total S on the analyzer Eltra CS 500, S-SO_4^{2-} in the water extract with the nephelometric method.

To define the statistic significance of the differences in the ground properties between two respective horizons in soil profiles, one-factor analysis of variance was carried out and SD was calculated ($\alpha = 0.05$).

3. Results and Discussion

The mean content of Ca, for all the studied ground samples was 45.11 g · kg^{-1}, there were however big differences between the studied plots and horizons in the profiles (Tabs 3, 4). The higher content of Ca, on average in the profile up to 70 cm depth, was in the areas of scarp, covered with forest – 51.43 g · kg^{-1} (38.49–72.7 g · kg^{-1}), arable grounds on the surface of the top plateau contained on average 38.78 g · kg^{-1} (34,32–41,93 g · kg^{-1}). This mainly proves differentiation of the formations building the horizons near the surface. Such, and very often even higher variability in the content of different components in the post-mining grounds is a common phenomenon [3, 11, 15, 16, 18]. A high differentiation also occurs between the studied horizons in the profiles. In case of all the studied surfaces the lowest content of Ca was in the 0–10 cm horizon. In deeper parts of the profiles there is a growing trend in the content of this element, which however is not so clear-cut, especially in the relationship to the area on the scarp (differences statistically not significant). The content of Ca in the grounds of 0–20 cm horizon on the plateau was on average 53.0 g · kg^{-1} before starting the remediation measures [10]. Now the grounds of all the horizons of studied surfaces on the top plateau and the majority of the horizons on the scarp, showed significantly smaller contents, which especially refers to horizon 0–10 cm (mean content 31.28 g · kg^{-1}).

The highest amount of calcium occurs in the form of $CaCO_3$, in the case of the covered with forest scarp; its fraction in the total content of this element on average ranges from 91.4% in 0–10 cm horizon to 76.4% in 50–70 cm horizon. In the case of agriculturally used plateau the participation of this form of calcium is slightly lower and on average ranges from 85.7% in 0–10 cm horizon to 64.03% in 30–50 cm horizon (Figs 1, 2).

However, the clear decreasing trend of this form of calcium deep down to the profile, occurred only in case of the arable land of the plateau. The level of the content of $CaCO_3$ in all the profiles and studied horizons should be regarded very favourable, taking into account its structure-forming and stabilizing impact on the reaction and the degree of the saturation of the sorption complex with alkalis [5, 13].

Table 3. The content of calcium and sulphur forms in forestry managed soil of the rubble heap "Machów"

Plot no.	Depth [cm]	Content of Ca forms			Content of S forms	
		total	Ca-$CaCO_3$	in H_2O	total	S-SO_4^{2-}
		[$g \cdot kg^{-1}$]				
1	0–10	60.03	57.0	0.293	2.59	0.01
	10–20	73.21	71.6	0.164	2.51	0.03
	20–30	62.89	56.8	0.214	0.80	0.11
	30–50	83.69	76.4	2.855	11.88	2.67
	50–70	83.69	58.0	2.838	6.56	2.55
2	0–10	35.30	28.8	0.274	5.23	0.08
	10–20	37.50	37.4	0.167	4.55	0.06
	20–30	39.11	36.8	0.174	3.85	0.06
	30–50	38.72	39.2	0.181	2.89	0.08
	50–70	41.83	36.4	1.357	5.00	1.23
3	0–10	36,50	34,8	0.209	7.17	0.07
	10–20	43.41	41.0	0.205	7.06	0.59
	20–30	41.95	39.2	1.161	8.64	0.98
	30–50	47.55	42.4	2.811	9.20	2.71
	50–70	46.14	36.8	2.787	14.75	2.71
Mean	0–10	43.94	40.2	0.259	4.99	0.05
	10–20	51.37	50.0	0.179	4.71	0.23
	20–30	47.98	44.27	0.516	4.43	0.34
	30–50	56.65	52.67	1.949	7.99	1.82
	50–70	57.22	43.73	2.327	8.77	2.16
$LSD_{\alpha=0.05}$		n.s.	n.s.	1.46	n.s.	1.16

Mean – arithmetic mean; n.s. – not significant differences.

Table 4. The content of calcium and sulphur forms in agriculturally managed soil of the rubble heap "Machów"

Plot no.	Depth [cm]	Content of Ca forms			Content of S forms	
		total	Ca-$CaCO_3$	in H_2O	total	S-SO_4^{2-}
		[g · kg^{-1}]				
4	0–10	32.93	29.00	1.50	6.80	1.33
	10–20	41.13	29.56	2.88	11.85	2.79
	20–30	43.36	32.92	2.95	11.60	2.80
	30–50	42.82	26.24	2.85	14.91	3.12
	50–70	40.17	29.00	2.72	12.01	3.14
5	0–10	27.14	22.32	0.97	4.33	0.76
	10–20	37.21	23.44	3.04	9.73	2.75
	20–30	34.75	19.52	2.89	16.78	2.79
	30–50	36.49	19.60	2.80	15.40	2.90
	50–70	36.02	22.40	2.68	13.51	2.99
6	0–10	33.76	29.12	2.55	4.95	2.38
	10–20	36.33	29.12	2.86	7.26	2.74
	20–30	38.20	26.88	2.76	14.41	3.14
	30–50	47.37	35.28	2.68	11.51	3.24
	50–70	54.01	40.32	2.53	14.46	3.53
Mean	0–10	31.28	26.81	1.67	5.36	1.49
	10–20	38.22	27.37	2.93	9.61	2.76
	20–30	38.77	26.44	2.87	14.26	2.91
	30–50	42.23	27.04	2.78	13.94	3.09
	50–70	43.40	30.57	2.64	13.33	3.22
LSD $_{\alpha=0.05}$		n.s.	n.s.	0.76	3.89	0.59

Mean – arithmetic mean; n.s. – not significant differences.

The content of water-soluble Ca shows small differentiation in the profiles of the agriculturally used land, except of horizon 0–10 cm, containing almost only a half of the Ca content 1.67 g · kg^{-1}, in the relation to deeper horizons. On average the highest content of Ca was in horizon 10–20 cm – 2.93 g · kg^{-1}. The lowest content of the soluble component is in the surface horizon and the highest in the horizon lying directly under it. This proves more difficult transportation of water and water-dissolved components down the profile. This is quite obvious, regarding the grain composition (very heavy formation), high fraction of swelling minerals (montmorillonite) in the ground and still relatively slow degree of advancement of the soil-making process.

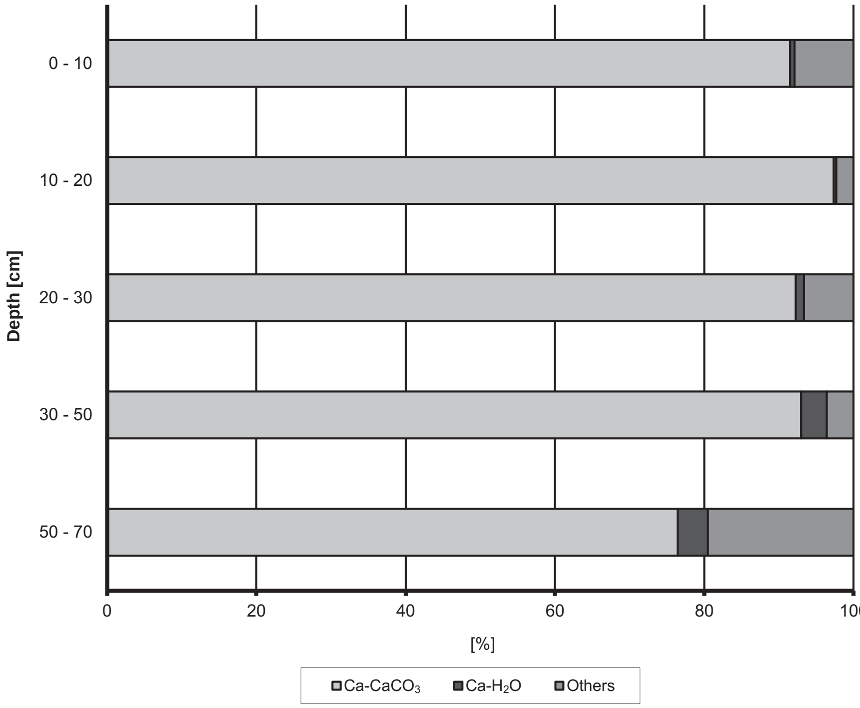

Fig. 1. The distribution of Ca forms in forestry managed soil of the rubble heap "Machów"

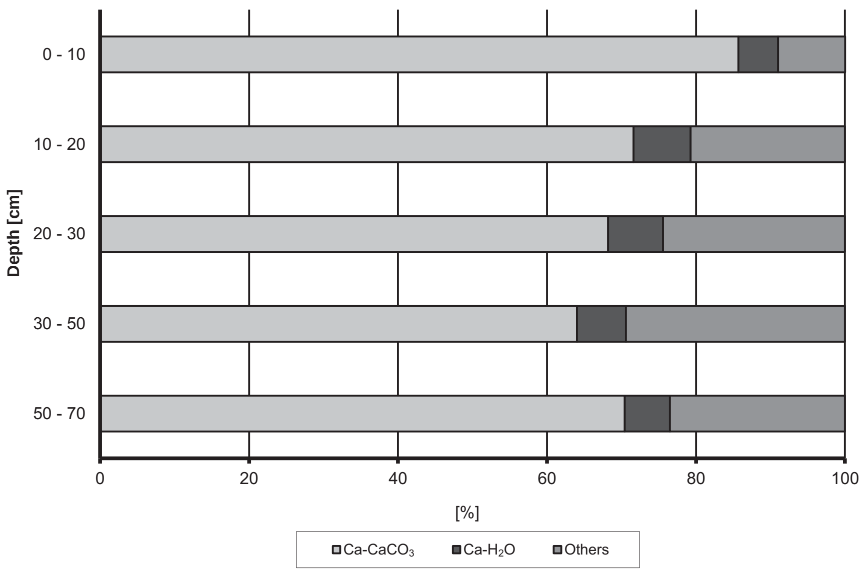

Fig. 2. The distribution of Ca forms in agriculturally managed soil of the rubble heap "Machów"

The situation in the case of the grounds of the forested scarp is different. In three surface horizons (to the depth of 30 cm) the content of the soluble form of this element was relatively low (usually below 0.5 g · kg^{-1}), several times lower than in deeper horizons and respective horizons of the arable areas. It indicates looser structure and consequently permeability of the grounds of forest-covered scarp to the depth of 30 cm. This is definitely the result of deeper penetration of the roots of trees and shrubs. Higher permeability of three surface horizons and intensive washing out the elements on the scarp is also indicated by the values of electrolytic conductivity (Tabs 1, 2). The mean content of sulphur for all the analysed samples of the ground is 8.74 g · kg^{-1}, there is however high differentiation of its content both between the studied plots, as well as within the profiles.

In the agricultural grounds on the plateau it is on average almost twice as big as on the scarp. Up to the depth of 20 cm its content is significantly lower than in 20–70 cm horizons. In the latter, the mean content was 13.84 g · kg^{-1} and it was only slightly lower than the content found in the grounds of the plateau before starting their management – 14.6 g · kg^{-1} [9]. In the profiles on the scarp generally two zones could be differentiated: Sog, zone of three horizons close to the surface (0–30 cm), with the content of 4.4–5.0 g · kg^{-1} and two deeper horizons (30–70 cm) of the content 8–8.8 g · kg^{-1}. The cause of twice as low mean content of sulphur in the profiles on the scarp in the compared to the grounds on the plateau, apart from the differentiation of the mineralogical composition of the formations, is undoubtedly the impact of a deeper root system of trees and shrubs, loosening ground and enhancing the microbiological activity and oxidation of reduced compounds of sulphur and then washing them out with water flowing down the scarp.

This is also indicated by the content S-SO_4^{2-} in the profiles on the scarp and the plateau. In both cases there is a growing trend for the studied plots down the profile, however, with a deep, often multiple differentiation of the content of this form of sulphur in respective horizons. In the grounds of the forested scarp to the depth of 30 cm, the content of sulphate sulphur, as well as its participation in the total content of sulphur are many times lower that in deeper horizons, and especially in 50–70 cm horizon (Tab. 3). The situation on the agriculturally used plateau is different. There the horizons in the depth ranging from 10 cm to 70 cm show similar contents oscillating around 3 g · kg^{-1}, only surface horizon (0–10 cm) usually contains less sulphur (statistically significant difference) – 1.5 g · kg^{-1} (Tab. 4). More dynamic and deeper transportation of both calcium and sulphur was found by Gołda [4] in long term studies on the agriculturally managed slimes after the flotation of sulphur ore, however, with significantly higher content of both elements. The proportion of S-SO_4^{2-} in total S in the grounds of the plateau is high and in all the horizons exceeds 20%, while in agricultural soils it is usually a few per cent [11, 13]. Intermediate (several per cent) participation of this form of sulphur was found by Gilewska and Spychalski [3] in the surface horizon of moderately compacted arable grounds of the Konin Mine spoil tip, however, with a much lower general content of sulphur in the grounds. The situation in the profiles of forested scarp is different. In its three upper horizons (up to 30 cm depth) this participation is about 5%, and grows with the depth and only in the deepest horizon is on the level closed to the plateau grounds.

The mole proportion of the total content of calcium to sulphur in the case of all the studied plots and horizons is greater than 2 (2.18–8.66), shows higher values in the horizons near the surface (Fig. 3). It is approximately higher in the whole profile of the forested scarp, compared to the agriculturally used plateau. This situation makes conditions for stable reaction in a long time perspective.

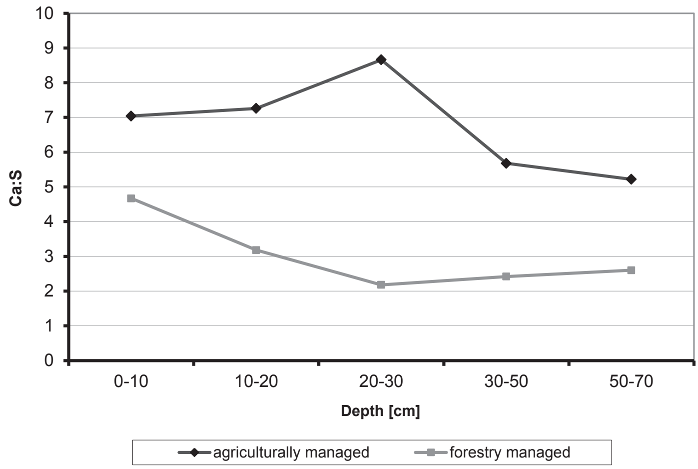

Fig. 3. Molar ratio of the total content of calcium to sulphur in the grounds of the rubble heap of the Sulphur Mine "Machów"

4. Conclusions

1. The thirty year period of forest and agricultural management caused a significant decrease in the content of different forms of calcium and sulphur only in the horizons near the surface, in the case of agricultural management – up to the depth of 20 cm, and in the case of the forest – 30 cm.
2. The content of calcium, especially $CaCO_3$, despite a small decrease, compared to the initial state, continues to be close to the contents optimal due to structure-forming and reaction stabilizing impact and the degree of saturation with the alkalis of the sorption complex.
3. The content of sulphur, both the total content, as well as sulphates continues to be high also in the horizons near the surface, where it decreased many times, compared to the initial state.
4. Many times higher mole content of calcium in the ground compared to sulphur guarantees the lack of thread related both to its high content and stability of the reaction in a long time perspective.

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