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Research Article

LIMING OF ACIDIC SOILS WITH BELITE SLUDGE

Aleksandr E. Isakov[1], Kseniia V. Barygina[1]

[1] Saint Petersburg Mining University, 21st line V.O., 2, 199106 Saint Petersburg, Russian Federation, e-mail: omnp@spmi.ru

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ABSTRACT
The metallurgical enterprises are a major source of large-tonnage industrial wastes containing valued components. A significant discrepancy between the volumes of waste formations and its utilisation leads to the necessity of large-scale sludge dumping. The article describes a recycling method for belite sludge that is the waste of the alumina production from nepheline concentrate. The physical and chemical properties of belite sludge were analysed and the conclusions about the possibility and outlook of its using as an ameliorant were drown. The main results show that adding the belite sludge to acidic soils provides a certain positive effect. The main conclusions allow to say that belite sludges are an ecologically safe substance that can be used as a liming material for acidic soils.

Keywords: belite sludge, nepheline sludge, liming, acidic soils, recycling, metallurgical wastes.

INTRODUCTION

Metallurgical enterprises produce, according to rough estimates, about 210 million tons of solid waste per year in the course of their activities, which is three quarters of the total processing industries waste [State, 2016]. This group of waste includes roasted products, dust, sludge, metallurgical slag (up to 15–25 tons in 1 ton of non-ferrous metal smelting).

Such wastes are mostly utilised for the production of construction materials. The priority of this utilisation type is motivated by the wastes specific properties and chemical composition, close to natural raw construction materials. Moreover, if the content of valuable components is sufficient, they are reextracted from the waste [Antoniadis et al., 2012; Shchukina et al., 2004; Simard et al., 1999].

There are two advanced methods of alumina production, which depend on the composition and properties of the base ore: sintering process (pyrometallurgical processing) and the Bayer process (hydrochemical method). Almost all alumina in the world is produced from bauxites of various mineralogical types [Loginova et al., 2015; Sushkov et al., 1957].

The insufficient reserves of bauxite ores in Russia forced the development and introduction of the alumina production from alternative raw materials. The production of alumina from nephelines makes economic sense only with complex processing with the market-ready by-products – soda, potash, cement. Alumina from nepheline In the Russian Federation is produced at two enterprises: BaselCement-Pikalevo LLC (PGK) and RUSAL Achinsk Alumina Refinery (AAR).

The belite (nepheline) sludge is the main waste type of such enterprises (according to rough estimates, about 100 million tons of sludge are stored in the AAR sludge dump, the sludge output per 1 ton of alumina is about 6 tons). The predominance of calcium and silicon compounds in sludge composition provides its successful use for the production of cement mixtures, silicate bricks, refractories, bottom enforcement of roadways [Antoniadis et al., 2007; Beloglazov et al., 2014; Ravich, 1988].

The sludge as a secondary material resource has a key role for the building industry. However, available technologies and a limited market, due to hard-to-reach location of mining areas, do not ensure the full sludge utilization.

METHODS AND MATERIALS

About 1.5 million tons of belite sludge per year is formed in the production of alumina at the BaselCement-Pikalevo LLC, most of which (from half to three quarters) goes to cement production.

Current research shows calcium oxides, silicon oxides and a certain set of additional compounds (Table 1) prevailing in the composition of belite sludge.

The phase composition is almost completely represented by belite, dicalcium silicate $\beta \cdot 2CaO \cdot SiO_2$, which crystal lattice incorporates such impurities as calcium oxide (CaO), silica (SiO_2), alumina (Al_2O_3), iron (III) oxide (Fe_2O_3) and other metal oxides. The granulometric composition of the sludge is characterized by homogeneity with the predominant fractions size of 0.5–1 mm (Table 2).

Belite sludge refers to the fifth Russian waste hazard class so that its disposal is not difficult. The high content of CaO and SiO_2 in the sludge is the reason for its wide use in the production of construction materials.

Table 1. Chemical composition of belite sludge

Element oxide	Concentration, wt%
CaO	58.75
SiO_2	32.53
Fe_2O_3	2.49
Al_2O_3	2.34
MgO	1.26
K_2O	0.81
Na_2O	0.81
TiO_2	0.22

Table 2. Granulometric composition of belite sludge

Grading fraction, mm	Concentration, %
<0.05	0.57
0.05–0.1	6.17
0.1–0.2	18.80
0.2–0.3	12.74
0.3–0.4	12.54
0.4–0.5	4.88
0.5–1	29.80
1–2	8.37
2–3	1.75
3–4	1.02
>4	3.23

The toxicity determination of sludge aqueous extract was determined by the biotesting method.

The analysis was carried out according to the procedure of «PND FT 14.1: 2: 3: 4.10–04 / 16.1: 2.3: 3.7–04 "Method for determination of toxicity of samples of surface unsalted, ground, drinking, and sewage waters, aqueous extracts from soil, sewage sludge and waste by a change in the optical density of the chlorella algae (*Chlorella vulgaris Beijer*)".

The technique is based on recording differences in the optical density of the chlorella algae test culture grown on a medium that does not contain toxic substances and test samples in which these substances can be present.

Before dilution, the pH of the extract should be adjusted to 7.5–8.0 by adding 10 % HCl.

A ten-fold number of dilutions were prepared for the analysis. Thus, the following 45 cm^3-samples, including a control one, were obtained:

1. Initial (not diluted) water extract, 100 %
2. The extract, diluted 10 times, 10 %,
3. The extract, diluted 100 times, 1 %,
4. The extract, diluted 1000 times, 0.1 %,
5. The extract, diluted 10 000 times, 0.01 %.
6. Control sample (distillate).

An algologically pure culture of *Chlorella vulgaris Beijer* in the exponential stage of growth was used for the biotesting.

Test algae culture with the volume of 2 cm^3 was added six times to glasses containing 48 cm^3 of control and test samples of water or waste extracts.

The content of each glass was poured in 6 cm^3-volume reaction bottles (4 bottles for each sample, including a control one; 24 cells total). The growth characteristics of the chlorella algae culture are determined in the multi-crop cultivator KVM-05. After cultivating for 22 hours, the optical densities of the solutions were measured to calculate the sample toxicity. The average optical density value was calculated for each dilution; the extreme minimum and maximum values were not considered.

The relative difference in the optical density was calculated for each dilution as compared with the control:

$$I = (Xc - Xe) / Xc \times 100 \%,$$

were: Xc and Xe are the average values of optical density in the control and in the experiment, respectively.

The measurement results of optical density and the percentage deviation are presented in Table 3.

The toxicity criterion for the aqueous extract is the decreasing average optical density in comparison with the control sample by 20% or more, or its increase by 30% or more.

If the toxicity criterion is not exceeded at any water dilution, including the original undiluted sample, the specimen is considered non-toxic. In this case, the maximum decrease in optical density is 18.3% that allows concluding that the aqueous extract is non-toxic.

RESULTS AND DISCUSSION

The use of belite sludge as a liming ameliorant is substantiated by its chemical composition and particle size distribution, as well as the accumulated experience of implementing similar industrial wastes. Natural materials containing calcium, such as lime, dolomite flour, and carbonic calcium gypsum, are used to reduce soil acidity. Metallurgical slag and ash-and-slag wastes, conversion chalk, and defecate are also used because of their similarity in composition and properties [Cehlár et al., 2016; Lavrischev et al., 2013; Orlov et al., 2002; Pavolová et al., 2016; Yanenkov, 2009].

The liming process takes place due to the displacement of the hydrogen ion from the soil absorbing complex, SAC [Orlov et al., 2002]:

$$SAC\text{-}H_2 + CaCO_3 = SAC\text{-}Ca + H_2O + CO_2$$

Natural materials containing calcium and magnesium in the form of carbonates and hydroxides are traditionally used to reduce soil acidity. The other compound, dicalcium silicate, makes up the bulk of belite sludge. Its liming action occurs due to the reaction of belite hydrolysis:

$$2(2CaO \times SiO_2) + 4H_2O = \\ = 3CaO \times 2SiO_2 \times 3H_2O + Ca(OH)_2$$

Belite makes up 80–85 wt% of a slag and is decomposed by water to form hydrated lime, which is also produced by water-reactive CaO admixture. H^+ and Al^{+3} ions are replaced in the soil absorbing complex by calcium lime when neutralising acidic soils.

It is known that the neutralising ability of hydrated lime is 1.35 higher than that of calcium carbonate; so that, lime is added in smaller quantities than carbonate. Moreover, the effect in this case takes place quicker [Alvarenga et al., 2008; Antoniadis et al., 2006; Alekseenko et al., 2016; Dyakonov, Anoshko, 1995].

That is confirmed by the alkaline reaction of aqueous sludge extraction. The pH 10.6 value was determined using a combined potentiometric titration electrode Aquaton ATP-02 and Titrate 5.0.

Radiometric measurements of the slurry were conducted using the MKS-AT1117M dosimeter-radiometer and showed no excess as comparing with the background. These measurements served as the basis for conducting field experiments. Soil of varying acidity was selected, each sample divided in half. Belite sludge was added to one of the samples. The experimental design is shown in Fig. 1.

The tested soil was selected in such a way that it was possible to evaluate the effect of belite sludge on various soil types. Two samples (1 and 2) are artificially transformed soils. These acidic soils were subjected to significant anthropogenic load. Soils 3 and 4 were not impacted significantly; their pH values are due to natural causes.

The quantity of liming substance is determined basing on soil pH and its particle size distribution. The latter is found by the wet method according to F.Ya. Gavrilyuk [Yaskov, 2009]. Soil characteristics are presented in Table 4.

The composition of the sown herbal mixture was chosen in such a way that the result was as clear as possible. So that, the selected plant varieties are sensitive to soil pH.

Table 3. Measured values of optical density

Analysis number	Control	Percentage of initial solution				
		100 %	10 %	1 %	0.10 %	0.01 %
1	0.131	0.104	0.120	0.121	0.125	0.129
2	0.136	0.110	0.118	0.121	0.120	0.131
3	0.131	0.110	0.130	0.120	0.121	0.151
4	0.131	0.140	0.120	0.109	0.125	0.130
Mean value	0.132	0.108	0.119	0.121	0.123	0.130
	0	18.3	9.8	8.8	7.2	1.7

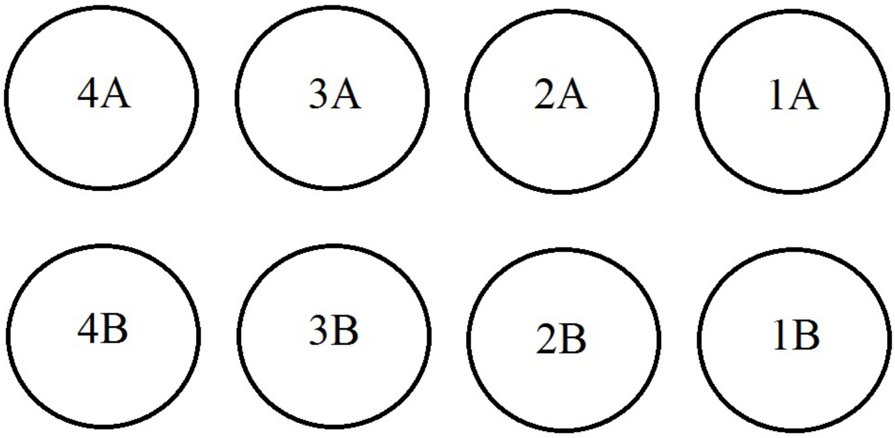

Fig. 1. 1–4 – various soil types; A – samples without addition of belite sludge; B – samples with addition of belite sludge

Table 4. Basic characteristics of soil samples

Sample number	pH of aqueous extract	Particle size distribution	Characteristics of soil sampling locations	Brief soil description
1	5	Sand	Roadside of a major highway	The soil is heavy, friable, the particles are dispersed. A huge amount of technogenic inclusions. Practically unvegetated on the surface. Soil organisms are almost not present.
2	5	Sandy clay	Roadside near a parking lot	The soil is rocky, hard, and lumpy; dense and viscous when wet. A huge amount of technogenic inclusions. Practically unvegetated on the surface. Soil organisms are almost not present.
3	6	Medium-textured loam	City park slightly influenced by vehicles and industrial enterprises	The soil is light, crumbly, and homogeneous. A dense plant cover, a highly developed root system. A small amount of technogenic inclusions. Soil organisms are present.
4	7	Heavy clay loam	Countryside, non-arable field	The soil is light, crumbly, and homogeneous. A dense plant cover, a highly developed root system. A huge amount of soil organisms. Technogenic inclusions are not present.

The following composition was chosen for the experiment: meadow fescue (*Festuca pratensis Huds*) – 35%, annual ryegrass (*Loliym multiflorum*) and pasture ryegrass (*L. perenne L.*)– 50%, meadow-grass (*Poa pratensis L.*) – 5%, white creeping clover (*Trifolium repens L.*) – 10%. The procedure for planting is shown in Fig. 2.

Regular monitoring of the growth of the herbal mixture was carried out for two months. Visual observation clearly showed more intensive growth of samples 1B, 2B, 3B, 4A. An example is shown in Figues 3–6: samples 10 days after the start of the experiment.

An assessment of the belite sludge effect on the growth of plants was based on experience of disturbed land reclamation in the Russian northern regions. Studies have shown that such indicators as the projective coverage of grasses and the dry weight of plants are the most characteristic for assessing the impact [Bezel' et al., 2007; Fauziah et al., 2011; Nakvasina et al., 2014; Pashkevich, Petrova, 2015; Tsadilas et al., 2009].

The projective coverage was measured using a Ramenskiy net. The generalised measurement results are shown in the diagram (Fig. 7). The results of measuring the dry mass of plants are shown in the diagram (Fig. 8).

CONCLUSIONS

A certain positive effect was found after adding the belite sludge to acidic soils in the course of the experiment. The projective cover of grasses in samples No 1–3 was 10–25% higher when using the sludge. At the same time, the projective cover had a 10 % decrease in the sample № 4 initially having a neutral reaction.

The similar results were obtained by measuring the dry mass of grasses: it had raised 1.5–2 times in acidic specimens as compared with those without additives; a two-fold decrease was marked in the sample 4B. It is worth noting that the weights of samples 1B and 2B differ significantly at the same acidity. This is due to the sandy composition of the sample № 1 and its excessively friable loose structure.

Basing on the qualitative and quantitative data on sludge composition, as well as on the results of the conducted experiment, it is possible to draw the following conclusions:

1. Belite sludges are an ecologically safe substance;
2. Belite sludges can be used as a liming material;
3. The best effect manifests when amending acidic soils (ph = 5);
4. The treated soil is to have a suitable texture and particle size distribution.

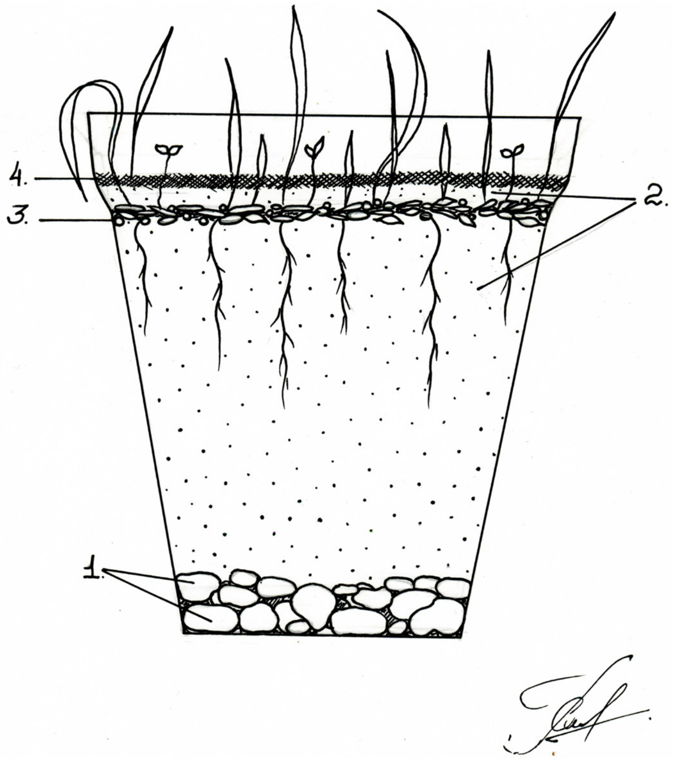

Fig. 2. Planting procedure; 1 – drainage layer; 2 – soil; 3 – herbal mixture; 4 – belite sludge

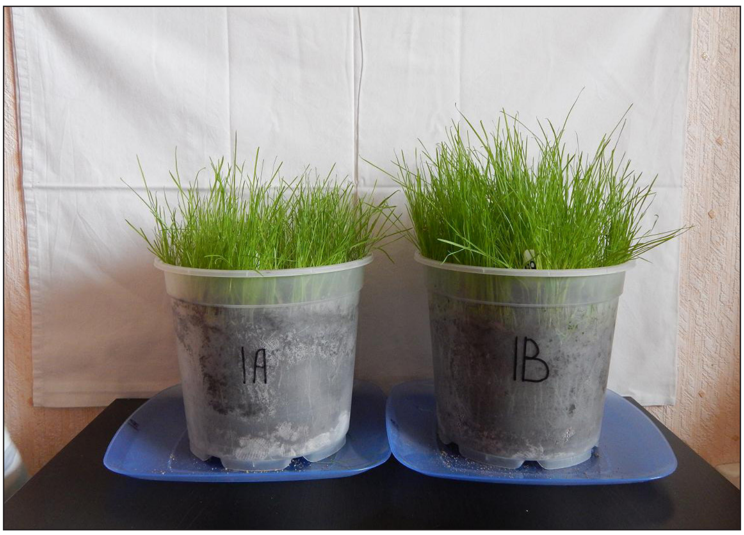

Fig. 3. Samples 1A, 1B

Fig. 4. Samples 2A, 2B

Fig. 5. Samples 3A, 3B

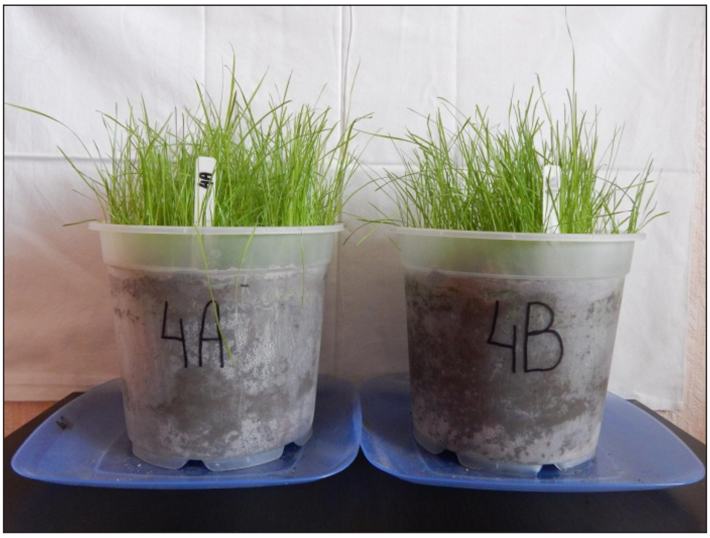

Fig. 6. Samples 4A, 4B

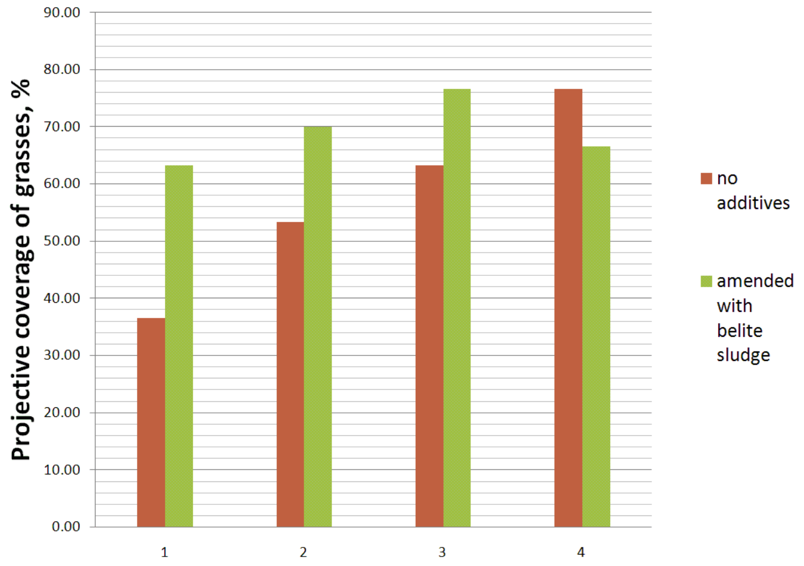

Fig. 7. Projective covering of grasses (samples 1–4)

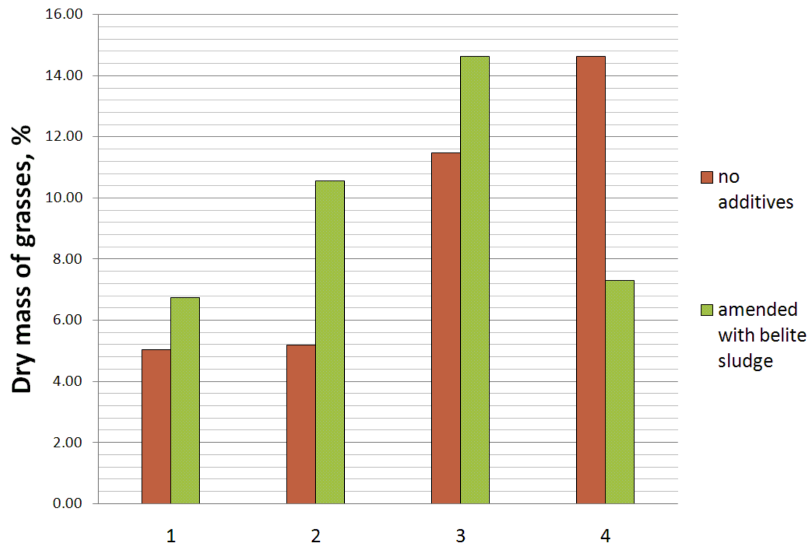

Fig. 8. Dry mass of grasses (samples 1–4

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