Environment Protection Engineering

Vol. 35 2009 No. 1

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USEFULNESS OF SELECTED MINERAL WASTES FOR RECLAMATION OF COPPER INDUSTRY DUMPING SITE

In the years 2007–2008, a potential utility of mineral wastes for reclamation of post-flotation sediment dumping site was tested. In the tests, use was made of barren rock, sand from a mine, overlay from a quarry, as well as phosphogypsum. They were used in the amount of 10% of sediment gravimetric capacity for pot experiments. Investigation proved that phosphogypsum and quarry overlay did improve those substrate properties which determine plant growth and development (pH and nutrient content). Additionally, phosphogypsum decreased the amount of substrate-soluble copper and zinc and, therefore, reduced their uptake by plants. According to the examination results, barren rock and mine sand considerably limited iron and manganese conversion into the forms easily assimilated by plants.

1. INTRODUCTION

In copper ore processing, there are produced a number of waste products which, apart from chemical compounds emitted into the atmosphere during flotation, are not suitable for a direct utilization and, therefore, stored on dumping grounds. Investigation has proved that these wastes have extremely disadvantageous properties which contribute to the pollution of both undeground and surface waters and to chemical alterations of soil and plants [1], [9]. The exploration of dumping sites in the region of Lower Silesia reveals that on those sites as much as between ten and twenty million m³ of organic, mineral and mineral–organic wastes are deposited. They can be utilized in reclamation of not used dumping sites. This process can involve the stabilization of waste dump surfaces, the reduction of erosion rate, then turfing and cultivation of appropriate plants [8].

The aim of the work was to assess the usefulness of some selected mineral wastes for revitalizing not used copper post-flotation sediment dumps located in Iwiny near Bolesławiec, in the region of Lower Silesia.

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2. MATERIALS AND METHODS

The investigation was conducted in the years 2007–2008 in a phytotronic chamber using the method of pot experiment. As a substrate we used a post-flotation sediment mixed with various kinds of wastes according to the following pattern:

A – post-flotation sediment + 10% of barren rock,
B – post-flotation sediment + 10% of mine sand,
C – post-flotation sediment + 10% of quarry overlay,
D – post-flotation sediment + 5% of phosphogypsum,
E – post-flotation sediment + 5% of mine sand + 5% of phosphogypsum,
F – post-flotation sediment + 5% of quarry overlay + 5% of phosphogypsum,
G – post-flotation sediment + 5% of barren rock + 5% of phosphogypsum.

Each experiment was carried out in four replications in 500 g capacity pots. A post-flotation sediment was thoroughly mixed with wastes and then basic nutrients were added in the following amounts:

N – 50 mg/pot, in the form of NH_4NO_3,
P – 30 mg/pot and K – 76 mg/pot, in the form of K_2HPO_4,
Mg – 20 mg/pot, in the form of $Mg\ SO_4 \cdot 7\ H_2O$.

The substrate prepared as above was sown with oats and its cultivation lasted 4 weeks, according to the method for this type of experiments. A 20% moisture of the substrate was maintained during plant growth and systematical observation of plant development was made. After harvesting we evaluated the yield of oat fresh mass and the yield of oat dry mass after its drying at the temperature of 105 °C. The material obtained was ground to determine the content of basic macrocomponents as well as microcomponents such as copper, zinc, manganese and iron. Substrate samples were collected from each pot and dried to measure their reaction as well as the content of phosphorus, copper, manganese and iron, as in the case of plant material. In order to determine the concentrations of the above elements, the plants were ashed at the temperature of 450 °C and then the ash obtained was digested in the concentrated HCl. After dissolving the residue in the solution of 1 mol dm^{-3} HCl, the phosphorus content was determined colorimetrically, while the remaining chemical elements were determined spectrophotometrically [7].

Soil pH was measured potentiometrically in 1 mol dm^{-3} KCl solution and soluble phosphorus was determined according to the Egner–Riehm method. Copper, zinc, manganese and iron were extracted with the solutions appropriate for these components. Of numerous commonly used in European Union extractions, we selected four, i.e. DTPA, $CaCl_2$, $Ca(NO_3)_2$ and Mehlich 3 solution. Quantitative determination of the elements was carried out by the method of atomic absorption, applying a flame technique with Varian Spectra AA 220 device.

3. RESULTS AND DISCUSSION

The analysis of chemical composition of post-flotation sediment showed its alkaline reaction [8] and a high content of easily soluble, thus easily accessible for plants, forms of potassium and magnesium, while phosphorus occurred in trace amounts. Waste product examined proved to contain various concentration of heavy metals, often considerably different from those occurring in the natural environment. There was detected high concentration of copper, cadmium, and nickel, while the content of zinc and manganese was similar to that commonly found in this type of wastes. These wastes affect in a different way not only the properties of post-flotation sediment, but also the oat chemical composition and yielding.

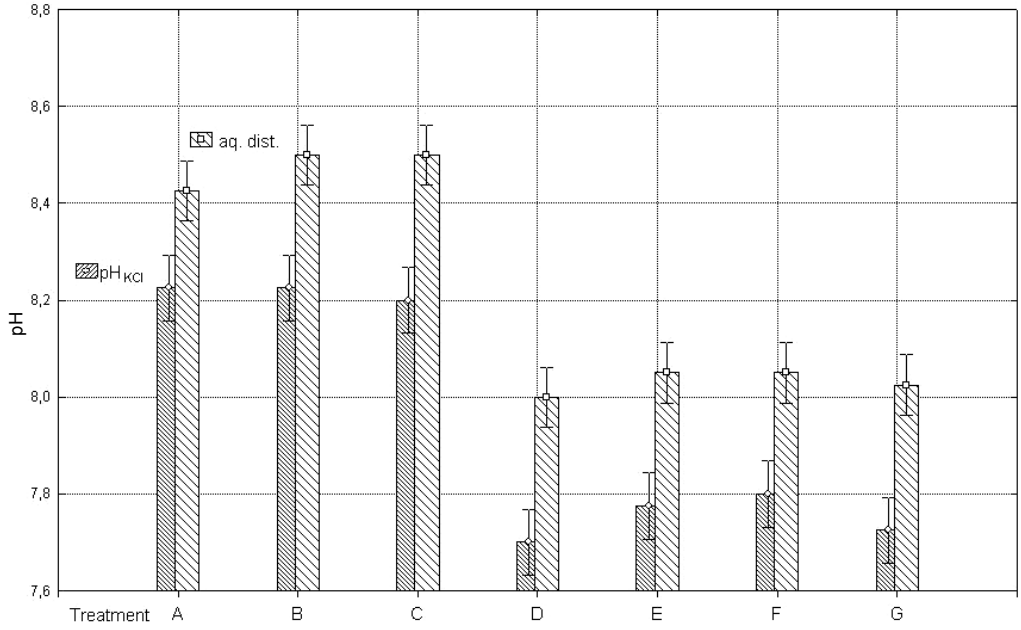

Fig. 1. Influence of waste type on soil reaction

The results shown in figure 1 prove that the wastes under examination, depending on their character, affected in different ways the substrate reaction. The least considerable influence had a barren rock, mine sand and weathered quarry overlay. The change in substrate reaction in this case was so slight that it actually remained alkaline. Similar results were also obtained by other authors [5] who a distinct lack in pH change explain by alkaline reaction of wastes themselves as well as by their slow reaction with post-flotation sediment.

The most significant, and at the same time the most advantageous for plant growth, change of substrate reaction was recorded after mixing post-flotation wastes with phosphogypsum, which resulted in the lowering of substrate reaction by as much as one pH unit.

Mineral wastes mixed with phosphogypsum in the proportion of 1:1 maintained that reaction at nearly the same level, useful for the cultivation of numerous plants. Many authors [1]–[3] confirm the results obtained by us, stressing that phosphogypsum adds acidity to its environment.

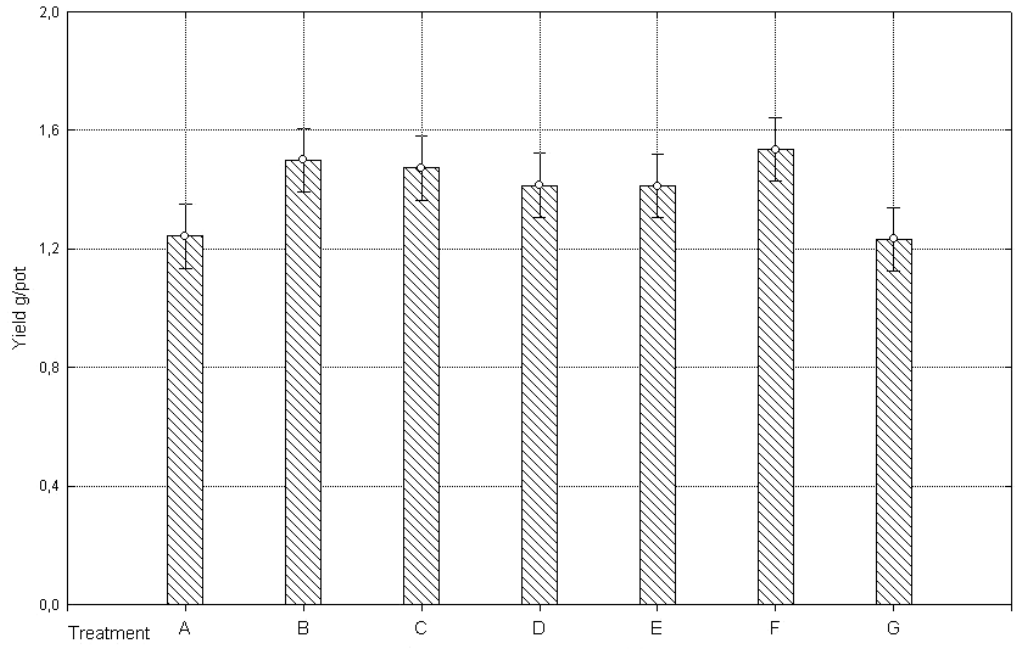

Fig. 2. Influence of waste type on oat yields

Oat yield in this experiment (figure 2) apparently correlated with substrate reaction and chemical composition of the wastes introduced. The lowest oat yield was recorded when barren rock, phosphogypsum and their mixture were added to post-flotation sediment, while the highest yield was obtained due to addition of pure weathered quarry overlay or its mixture with phosphogypsum.

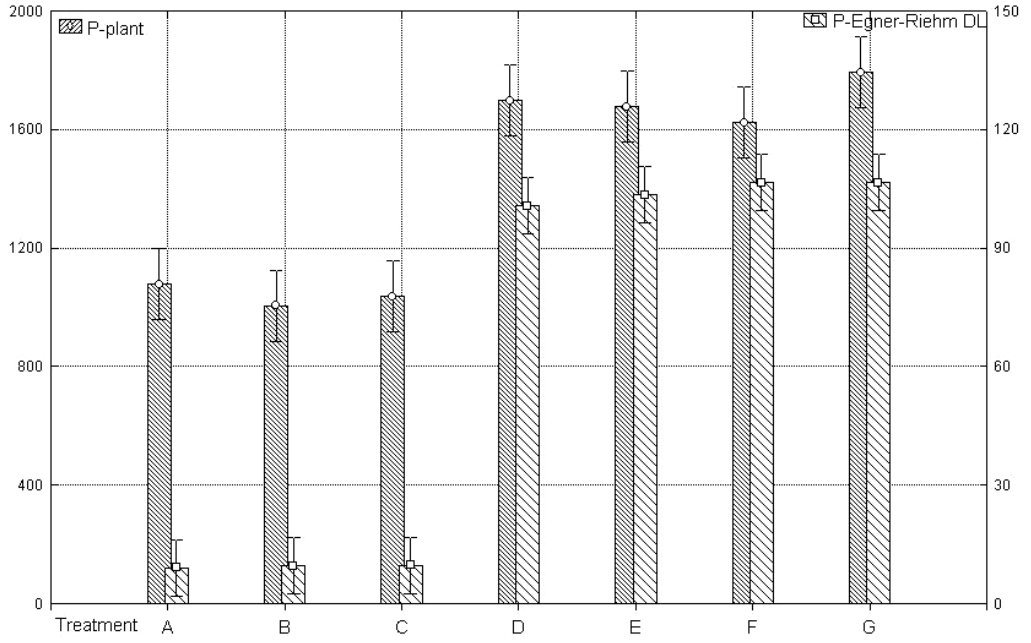

Fig. 3. Content of phosphorus in oat plants and in substrate (mg kg^{-1}d.m.)

Phosphorus is a very important component, as it improves both substrate properties and plant growth. In this investigation, active phosphorus was determined in a buffered solution of calcium lactate, hence in its most mobile form in substrate, easily assimilable by plants. Though a post-flotation sediment was mixed with mineral wastes, phosphorus content only slightly increased (figure 3). A considerable increase in the phosphorus concentration was recorded after sediment enrichment with phosphogypsum, both pure and mixed with sand, barren rock or quarry overlay. This enrichment also contributed to a significantly higher uptake of this nutrient from substrate by oats compared to the amount assimilated by plants cultivated on the substrate lacking in phosphogypsum. On the other hand, the plants grown on such a substrate assimilated a considerable amount of phosphorus probably due to the use of K_2HPO_4 fertilizer as a source of phosphorus [5].

Some authors [2], [4] believe that a decisive role in the reclamation of waste dump plays those additions which, apart from altering physicochemical properties of post-flotation sediment, provide the substrate with nutrients necessary for potential plants and do not contain any toxic elements. Quarry overlay is characterized by such properties, as its reaction is acid and it contains considerable amounts of nutrients and heavy metals in low concentration.

For the purpose of this work we selected some heavy metals, i.e. copper, zinc, manganese and iron, occurring in the substrate in the highest concentrations. Since the

concentrations of these metals determined in four extracting solutions proved that their uptake by oats is correlated, to the highest degree, with the metal concentrations in the DTPA extracting solution, all remaining relations were referred solely to this solution (the table).

Table

The coefficients of correlations between the content of Cu, Mn, Zn, Fe in substrate and plant

Substrate concentration	Plant			
	Cu	Mn	Zn	Fe
Cu_{DTPA}	0.523**			
Mn_{DTPA}		0.857**		
Zn_{DTPA}			–0.1643	
Fe_{DTPA}				0.498**
Cu_{CaCl_2}	0.009			
Mn_{CaCl_2}		0.688**		
Fe_{CaCl_2}				0.159
Zn_{CaCl_2}			–0.394*	
$Cu_{Ca(NO_3)_2}$	–0.039			
$Mn_{Ca(NO_3)_2}$		0.895**		
$Fe_{Ca(NO_3)_2}$				–0.107
$Zn_{Ca(NO_3)_2}$			–0.1091	
Fe_{M3}				–0.435*
Zn_{M3}			0.338	
Cu_{M3}	–0.499**			
Mn_{M3}		–0.326		

** $p < 0.001$; * $p < 0.05$

The concentration of copper dissolved in DTPA (figure 4) was the highest when mineral wastes added to the sediment constituted 10% of its gravimetric capacity. The lowest concentration of copper was detected in the substrates enriched with the mixture of mine sand, quarry overlay and phosphogypsum. Copper uptake by plants depended on substrate reaction as well. Oats absorbed this metal most easily at the highest pH, which confirms a widely known thesis that low reaction is responsible for releasing copper forms assimilable to plants which leads to an excessive accumulation of this element both in roots and in overground parts of plants [2], [6].

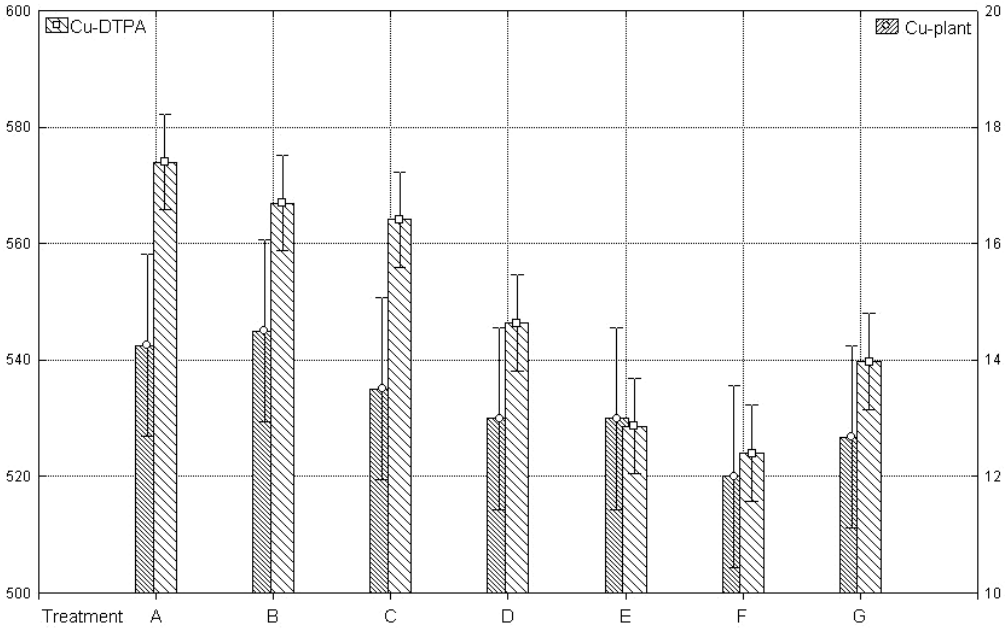

Fig. 4. Content of copper in oat plants and in substrate (mg kg^{-1}d.m.)

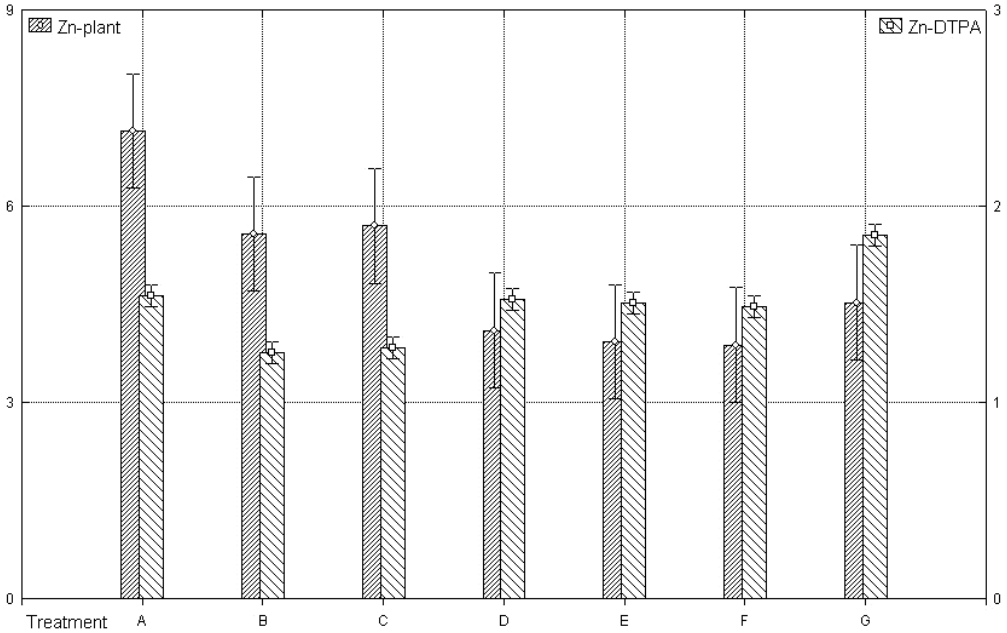

Fig. 5. Content of zinc in oat plants and in substrate (mg kg^{-1}d.m.)

Zinc content in substrate was dependent on waste chemical composition only to a low degree, which is shown in figure 5, as this content was very similar in all experimental substrates. The plants accumulated this metal most easily when they grew on mine sand, barren rock and quarry overlay.

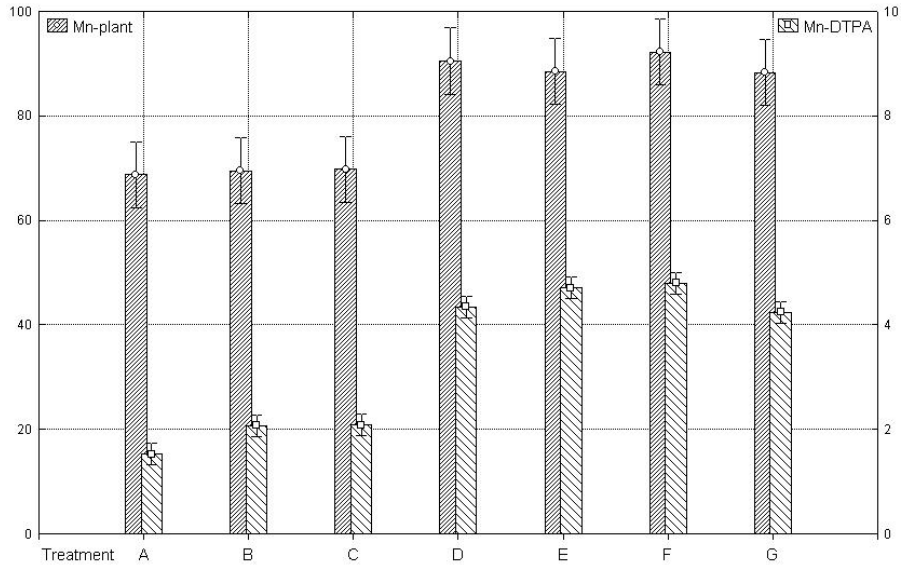

Fig. 6. Content of manganese in oat plants and in substrate (mg kg^{-1}d.m.)

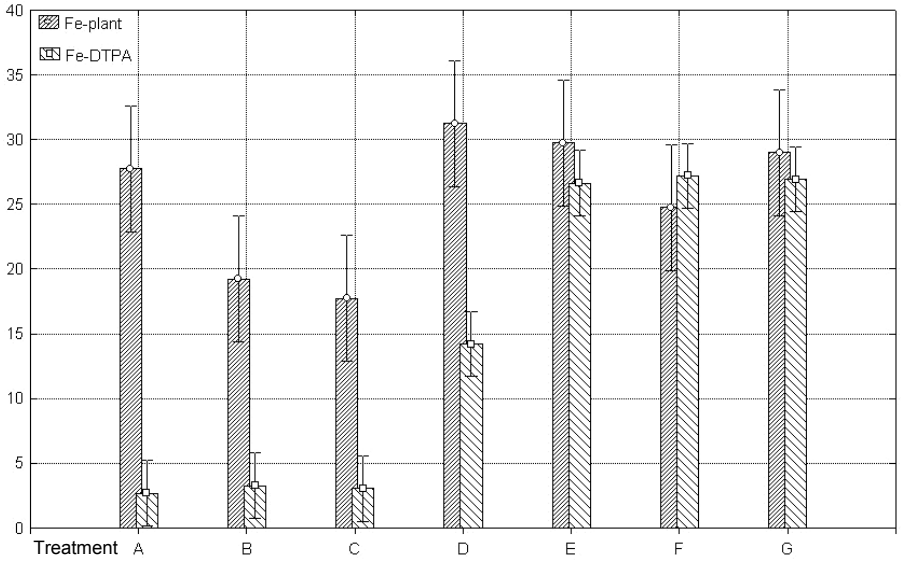

Fig. 7. Content of iron in oat plants and in substrate (mg kg^{-1}d.m.)

A slightly different pattern was followed in the case of manganese and iron which is shown in figures 6 and 7. The highest concentrations of those metals were determined where the waste used decreased the substrate reaction, while their lowest concentrations occurred when substrate reaction remained unchanged in spite of the additions introduced. The results obtained in this investigation confirm the thesis presented by other authors [4], [5] that manganese and iron in acid environment occur in the reduced, therefore easily soluble and assimilable forms. Our examinations also proved that at lower reaction of substrates the plants uptook these two metals in higher amounts, which was proven by their high concentration in the oats harvested. Nevertheless, we found the fact that alkaline reaction of substrates also results in relatively lower but still considerable concentration of manganese and iron in overground parts of plants quite alarming.

4. CONCLUSION

1. Phosphogypsum proved to be the most useful waste for pH control in post-flotation sediment.

2. The best conditions for plant growth and development occurred when post-flotation sediment was treated with quarry overlay, both using its pure form and that mixed with phosphogypsum.

3. Phosphogypsum proved to be the waste that allowed copper and zinc content to be decreased to the level safe for plant growth.

4. All the wastes examined modified iron and manganese content in post-flotation sediment; phosphogypsum in the mixtures with other wastes significantly increased concentration of these metals.

5. Of macronutrient indispensable for plants growth only phosphorus content depended on the wastes added. Phosphogypsum had an advantageous effect on this element content, raising its level to the values required by plants.

6. The results obtained proved that on post-flotation sediment dumping site it is possible to produce a fertile soil through agricultural measures, but further detailed research should be undertaken in this field.

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OCENA PRZYDATNOŚCI WYBRANYCH ODPADÓW MINERALNYCH DO REKULTYWACJI SKŁADOWISKA ODPADÓW Z PRZEMYSŁU MIEDZIOWEGO

W latach 2007–2008 badano możliwości wykorzystania odpadów mineralnych do rewitalizacji składowiska odpadów poflotacyjnych. W badaniach wykorzystano skałę płoną, piasek z kopalni, nadkład z kamieniołomu oraz fosfogips, które stosowano w doświadczeniach wegetacyjnych w ilości stanowiącej 10% objętości wagowej osadu. Badania wykazały, że fosfogips oraz nadkład z kamieniołomu w największym stopniu poprawiały te właściwości podłoża, które determinują wzrost i rozwój roślin (pH i zawartość składników pokarmowych). Fosfogips dodatkowo zmniejszał ilości miedzi i cynku rozpuszczalnego w podłożu, a tym samym ograniczał pobieranie tych metali przez rośliny. Badana skała płona i piasek z kopalni w znacznym stopniu ograniczały przechodzenie żelaza i manganu w formy przyswajalne przez rośliny.