*Polish J. of Environ. Stud. Vol. 20, No. 2 (2011), 351-354*

*Original Research*

# Possibility of Using Waste from the Polyvinyl Chloride Production Process for Plant Fertilization

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*Received: 2 August 2010*
*Accepted: 29 October 2010*

## Abstract

The aim of our research was to determine the potential of waste generated during the production of chlorine for the synthesis of polyvinyl chloride as plant fertilizer in agriculture. For the production of fertilizer sludge produced when cleaning the saline solution, 78 vol % waste sulphuric acid from the dehydration of chlorine and calcinated magnesite were used. The product contains minimum: MgO – 16%, CaO – 9%, $SO_3$ – 35%, and about 32% of water, mainly crystalline. The effect of the product on agrochemical properties of soil and crops was investigated in pot and field experiments. Soil fertilization with the product had a positive effect on the soil content of available magnesium and sulphate sulphur, their content in air-dry matter of plants and yields of spring rapeseed, and sugar beet roots.

**Keywords:** polyvinyl chloride, waste, plant fertilization, soil agrochemical properties, yield and quality of crops

## Introduction

Waste includes substances and objects defined in the Annex to Waste Law of April 27, 2001, with further amendments [1]; the keeper disposes, intends to dispose, or is obliged to dispose. Municipal and industrial waste is produced in big quantities, especially in highly developed countries. Adequate waste management is a serious challenge for contemporary societies. It needs legal and organizational standardization [2, 3]. According to the Decree of the Minister of the Environment of September 27, 2001 [4], waste depending on the criterion of the place it has been generated is classified into 20 groups. Much of it covers waste from different branches of industry, including the alkali and chlorine industries.

Chlorine is widely applied in the synthesis of organic and inorganic compounds, mainly polyvinyl chloride. On the industrial scale it has been produced since the end of the 19th century. PVC was detected in the late 19th century, but the material was not suitable for use. Industrial production was developed in the 1920s by Waldo Semon at Goodrich, but real production started during WW II. The biggest chlorine producer in Poland is Zakłady Azotowe ANWIL S.A. in Włocławek, the production of which involves the application of diaphragm technology (for $Cl_2$ production). Irrespective of the kind of the technology, it involves several stages: preparation and cleaning of saline solution, electrolysis of saline solution, drying and chlorine liquefaction, producing and concentration of soda lye. In the production process, besides chlorine and soda lye, also waste products are produced. Sludge obtained from cleaning saline solution includes precipitated calcium and magnesium ions in a form of calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$). The chlorine drying stage has accumulated used sulphuric acid [5, 6].

For waste management different recycling and disposal processes are in use [7-9]. One of the methods is to use specific fractions or types to fertilize soil. For that purpose,

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there is not only organic rich waste, e.g. agricultural, or the putrescible fraction of municipal waste [10, 11], but also other waste from different fields of commerce and industry. To produce fertilizers one may also use some waste: sulphuric acid [12], sodium sulphate [13], and magnesium salts [14]. The produce of fertilizers from waste has good ecological and economical aspects.

The aim of the present research was to determine the potential of waste from the production of polyvinyl chloride to produce fertilizers for agriculture.

## Materials and Methods

The waste used for the production of a fertilizer was sludge from cleaning saline solution and sulphuric acid produced in Anwil in Włocławek during the production of chlorine for the synthesis of polyvinyl chloride. Sludge precipitated from the solution of sodium chloride contains mainly: calcium carbonate, magnesium hydroxide, residual NaCl, and water. Concentrated sulphuric acid used to dewater chlorine is converted into waste acid of 78 vol %.

In the laboratory of PPHU Pro-Lab sp. z o.o., Anwil Group, a technological process has been developed in which the calcinated magnesite and waste from the chlorine production was used to produce a granulated product demonstrating properties of mineral fertilizer (Table 1).

In the present research the effect of the fertilizer obtained in such a way on agrochemical properties of soil and crops was evaluated. The research was performed in two stages. The first stage involved the single-factor pot experiment set up as a completely randomized design, in six replications. The experimental factor was made by the fertilizer produced from waste. To the 10 $dm^3$ pots filled with soil (Albic Luvisol) of 1.5 density, $Mg \cdot m^{-3}$ amount of 1.5 g of fertilizer was added per pot, which corresponded to a dose of 300 $kg \cdot ha^{-1}$ placed in 20 cm arable layer of soil in field conditions. The control was made up by pots filled with soil without fertilizer. Soil in both pot groups was incubated for 8 weeks, maintaining its moisture at 60% of the field water capacity. After 2 and 8 weeks of incubation soil was sampled. The following parameters were determined in the soil samples: $pH_{KCl}$, the content of the available forms of phosphorus, potassium, magnesium, and sulphur in sulphate form.

Table 1. Compounds of sludge and chemical composition of fertilizer product.

| Sludge | | Fertilizer | |
|---|---|---|---|
| Compound | % | Chemical composition | % |
| $CaCO_3$ | 37.3 | MgO | 16.0 |
| $Mg(OH)_2$ | 18.5 | CaO | 9.0 |
| NaCl | 7.4 | $SO_3$ | 35.0 |
| $H_2O$ | 28.1 | $H_2O$ | about 32% (crystalline) |

The second research stage involved single-factor field experiments set up as randomized blocks in four replications. The experiments were performed at the experiment station of the Faculty of Agriculture and Biotechnology at Mochełek (53º12'N, 17º51'E) at the University of Technology and Life Sciences in Bydgoszcz and on a partner farm. The region is characterized by low rainfall (450 mm annually). The research involved two crops of relatively high nutrition requirements (magnesium and sulphur): spring rapeseed and sugar beet. The spring rapeseed experiment was made on Albic Luvisol, of the good rye complex, and with sugar beet on Haplic Cambisol, of the good wheat complex. At both locations the content of magnesium available in soil ranged from low to average, and sulphur in sulphate form did not exceed 15 $mg \cdot kg^{-1}$ of soil. The experimental factor, with three levels, was the fertilizer obtained from waste applied to soil prior to plant sowing. The fertilizer was applied in spring at doses of 200 $kg \cdot ha^{-1}$ and 400 $kg \cdot ha^{-1}$, and then mixed with pre-sowing agricultural practices with soil. In the third level, the control, no fertilizer was used. The other elements of agrotechnical practises were compliant with the principles of the technology of cultivation of those crops. Over the period of intensive growth BBCH 50-53 (budding stage) – rapeseed and BBCH 40-43 (vegetative stage) – beetroot, leaves were sampled. In the leaves the following parameters were determined: the content of magnesium, total sulphur and nitrogen. At the BBCH 89 phase (ripening) there spring rapeseed and at the BBCH 49 phase – sugar beet roots were collected. The yields were expressed in $t \cdot ha^{-1}$. In the rapeseed the content of crude fat and in sugar beet roots the content of sugar and molasses-producing compounds were analyzed.

Chemical analyses of soil and plant material were made with the methods applied in chemical-agricultural research. The quality of sugar beet roots was evaluated on the Venema line, the theoretical expenditure of sugar was calculated according to the Reinefeld formula [15, 16], the content of crude fat with the Soxhlet extraction method, and total protein with the Kjeldahl distillation method (Nx6.25).

The data of analyses and measurements showing normal distribution were statistically verified. The analysis of variance (test F) was calculated, and the significance of differences was evaluated with the Tukey test at significance p=0.05.

## Results and Discussion

The product obtained from waste after the production of chlorine, similar to other products after the disposal of chemical waste containing magnesium salts [17], can be full-value mineral fertilizer. Placed in soil, already after two weeks of incubation a significant increase in the content of the forms of magnesium and sulphur available to the plants (Table 2) were identified. This increase, as compared with the control, was 5.8 mg $Mg \cdot kg^{-1}$ of soil and 7.1 mg $S_{SO_4} \cdot kg^{-1}$ of soil, respectively. After successive 6 weeks the increase in the content of available magnesium and sulphur was no longer high, with – 1.3 $mg \cdot kg^{-1}$ of soil for each of the nutrients.

Table 2. Agrochemical soil properties after 2 and 8 weeks of fertilizer incubation.

| Soil property | 2 weeks | | 8 weeks | |
|---|---|---|---|---|
| | Fertilizer dose (g per pot) | | | |
| | 0.0 | 1.5 | 0.0 | 1.5 |
| Magnesium (mg Mg·kg$^{-1}$ soil) | 24.0 b* | 29.8 a | 24.0 b | 31.1 a |
| Sulphur (mg $S_{SO_4}$·kg$^{-1}$ soil) | 14.3 b | 21.4 a | 14.0 b | 22.7 a |
| Phosphorus (mg P·kg$^{-1}$ soil) | 91.3 a | 90.5 a | 89.1 a | 93.6 a |
| Potassium (mg K·kg$^{-1}$ soil) | 166.2 a | 175.2 a | 5.7 a | 5.2 a |
| $pH_{KCl}$ | 5.8 | 5.8 | 5.8 | 5.9 |

*Different letters indicate there is significant difference between data on different columns.

Table 3. Content of magnesium, sulphur and nitrogen in leaves, as well as spring rapeseed and sugar beet yields.

| Feature | Spring rapeseed | | | Sugar beet | | |
|---|---|---|---|---|---|---|
| | Fertilizer dose (kg·ha$^{-1}$) | | | | | |
| | 0 | 200 | 400 | 0 | 200 | 400 |
| Magnesium (Mg % d.m.) | 0.21 c* | 0.23 b | 0.26 a | 0.78 b | 0.79 b | 0.82 a |
| Sulphur ( S % d.m.) | 0.55 b | 0.58 b | 0.62 a | 0.41 b | 0.41 b | 0.45 a |
| Nitrogen ( N % d.m.) | 4.03 a | 4.06 a | 4.01 a | 3.63 a | 3.59 a | 3.71 a |
| Seed yield (t·ha$^{-1}$) | 2.64 b | 2.97 a | 2.93 a | - | - | - |
| Root yield (t·ha$^{-1}$) | - | - | - | 68.4 b | 70.9 b | 75.2 a |

*Different letters indicate there is significant difference between data on different columns.

However, there was no effect of the fertilizer on the content of plant available phosphorus and potassium found in soil and on the pH of the soil. In the pot experiment reported by Tkaczyk and Chwil [18], magnesium sulphate did not change the soil pH, but its content of phosphorus determined with the Egner-Riehm method did increase.

The fertilizer applied pre-sowing affected the chemical composition of leaves and the yields of spring rapeseed and sugar beet (Table 3). The content of magnesium in spring rapeseed leaves increased with an increase in the fertilizer dose. A significant increase in the content of magnesium in sugar beet leaves and sulphur in both crop species occurred only after the application of fertilizer at a dose of 400 kg·ha$^{-1}$. The contents were at a level considered average for the rapeseed leaves [19] and higher than average in sugar beet over intensive growth [20]. In sugar beet in the present research only leaf blades were sampled for analysis and not the whole leaves with petioles, which could have increased the content of nutrients in the dry matter of these organs. The fertilizer, however, did not change the content of nitrogen in leaves of both crop species, although other reports point to a significant relationship between fertilization with different forms of sulphur and magnesium and nitrogen management in plants [21, 22].

Fertilization, especially with nitrogen, is a basic agrotechnical factor of plant yielding. It affects both the yield and the plant's quality [23, 24]. The investigated fertilizer not containing nitrogen in its chemical composition, but containing magnesium, sulphur and calcium, had a favourable effect on the spring rapeseed and sugar beet yields. The increase in yields accounted for 12.5% of the rapeseeds following the application of 200 kg of the fertilizer per ha and for 9.9% of the beet roots after the application of 400 kg·ha$^{-1}$.

We also found a favourable effect of the fertilizer on some characteristics of the technological quality of spring rapeseed and sugar beet yields (Table 4). As a result of the application of the fertilizer, the content of crude fat in spring rapeseeds increased by 1.0-1.7 percentage points, at an unchanged content of total protein. An important change in the quality of sugar beet roots was the decrease in the content of potassium and a clear trend of increasing the content of sugar as well as theoretical sugar expenditure.

## Conclusion

The waste generated while producing polyvinyl chloride at the stage of production of chlorine in a form of sludge after cleaning saline solution and sulphuric acid, 78% can be used for the production of mineral fertilizer. The product obtained in PPHU ProLab sp. z o.o. used to fertilize soil increases its

Table 4. Spring rapeseed and sugar beet yield quality.

| Character | Fertilizer dose (kg·ha$^{-1}$) | | |
|---|---|---|---|
| | 0 | 200 | 400 |
| Content of crude fat in rapeseeds (% d.m.) | 42.3 b* | 43.3 a | 44.0 a |
| Content of total protein in rapeseeds (%) | 21.5 a | 21.5 a | 21.1 a |
| Content in sugar beet roots: | | | |
| - sugar (%) | 17.8 a | 17.8 a | 18.1 a |
| - α-amino nitrogen (mmol·1000 g$^{-1}$ of pulp) | 17.6 a | 17.6 a | 17.3 a |
| - potassium (mmol·1000 g$^{-1}$ of pulp) | 44.6 a | 42.9 a | 41.8 b |
| - sodium (mmol·1000 g$^{-1}$ of pulp) | 4.2 a | 4.3 a | 4.2 a |
| Theoretical expenditure of sugar (%) | 16.6 a | 16.6 a | 17.0 a |

*Different letters indicate there is significant difference between data on different columns.

content of available magnesium and sulphur does not act as an acidifier. Applied as a fertilizer of plants showing high magnesium and sulphur requirements, it demonstrated a favourable effect on the content of those nutrients in leaves, the yield of spring rapeseeds and sugar beet roots, as well as some technological quality characteristics of the yields.

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