# STABILIZATION AND REVEGETATION OF METAL SMELTER WASTES IN POLAND[1]

by

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Abstract. Water and wind erosion of toxic zinc and lead smelter waste is one of the most urgent environmental problems to be solved in the Silesia region of Poland. Over 87 million Mg of these materials were disposed of in uncontrolled piles leading to soil, water, and air pollution in extensively populated areas. Welz and Doerschel process Pb/Zn smelter wastes were stabilized in the summer of 1994 by application of heavy loads of calcium carbonate (30 Mg/ha), calcium oxide (1.5 - 15 Mg/ha), and municipal sewage sludge (150 - 300 Mg/ha), followed by seeding with a mixture of acid- and salt-tolerant grass species selected in a pot experiment. Vegetation was successfully established on 85% of the Welz material demonstration plot area (0.5 ha), even though it was initially high in water-soluble zinc, lead, and cadmium ranging from 0.4 to 1311, 0.1 to 5.8, and 0.05 to 55 mg/kg, respectively. Standing biomass approached 2.0 to 2.5 Mg/ha on the stabilized Welz waste at the end of the second growing season. Laboratory experiments demonstrated that amendments with CaO can effectively reduce metal solubility to ppb levels in the wastes. However, the use of $CaCO_3$ (up to 10% w:w), due to limited solubility and occlusion with metal hydroxides, allowed phytotoxic levels of zinc (30 mg/l) and cadmium (1.7 mg/l) in soil solution. The revegetation of much of the Doerschel material area failed because of extremely high salinity (16 dS/m), high content of water soluble metals (Cd in particular), and heavy compaction. The area was capped with waste lime and retreated with sludge (300 Mg/ha) in 1995, and preliminary results indicate greater success at stabilizing this exceptionally harsh material. The observed plant response to sludge and lime indicates this approach to be an environmentally beneficial technology as compared to the traditional methods utilizing topsoil covers or heavily engineered material processing or encapsulation approaches.

Additional Key Words: Sewage Sludge, Lime, Salinity, Potential Acidity, Topsoiling.

## Introduction

The Upper Silesia region (Gorny Slask) is located in southwestern Poland. Although it occupies only about 2% of Poland's territory, it is home to over 10% of the country's population and is the nation's main industrial center. It has rich deposits of coal, zinc and lead. Today it is a vast agglomeration of mines, steel works, smelters, chemical plants and other industries. The City of Katowice (population 380,000) is the political center of the District which covers 14 cities and a number of neighboring towns which merge into a large metropolitan area with a population over three million. It is one of the biggest industrial centers in Europe and one of the most outdated.

Waste disposal in industrialized areas of eastern and central European countries has been a serious environmental issue for decades. The Katowice District in Upper Silesia is a typical example of the environmental consequences caused by uncontrolled industrial activity with little or no effort to protect the environment (Ochrona, 1993). This history is reflected in heavy soil, water, and air pollution that is incomparable to any other region in Europe. During the last few years, this situation has been improving due to a significant reduction of the amount of industrial pollutants emitted to the environment. These positive trends are related not only to the changes in the structure of heavy industry that have eliminated the most environmentally damaging processes, but also to the introduction of control devices and environmental law enforcement. However, very little progress has been achieved regarding waste disposal problems. Thousands of industrial and mining waste piles are concentrated in a very limited area. It has been estimated that over 90% of

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the solid waste material produced by the entire heavy industry and mining sector in Poland has been deposited in Upper Silesia. A small percentage of these sites, particularly coal processing waste dumps, have been reclaimed by the use of thin topsoil lifts (30 cm) to cover the fill surface. However, this traditional method, however, is extremely expensive, and not always successful (Patrzalek and Strzyszcz, 1980; Strzyszcz, 1980). The majority of mining waste sites are potentially phytotoxic and very difficult to revegetate by traditional means. As a result, large areas of mining wastes remain exposed to wind erosion and to the runoff or leaching of toxic constituents following rain or snowmelt. Therefore, the prevention of losses of metalliferous dust to the surrounding community coupled with minimization of direct contact by childern playing on the piles have become major priorities for the local environmental protection units. The ground-water beneath these waste piles and associated metal mine workings has been extensively contaminated with metals and acidity, and has generally been deemed "beyond renovation". Therefore, there is an urgent need to begin an extensive region-wide reclamation program based upon technologies successfully applied in different countries experiencing similar problems.

Due to the change in socio-political structure and the associated emphasis on cleaning up surface waters, 30 new wastewater treatment plants will be constructed in Upper Silesia by the year 2000 and will increase the sludge quantity from current levels (40,000 Mg/yr) to > 100,000 Mg/year. While this provides an obvious solid waste disposal challenge, it also could simultaneously provide an opportunity for reclaiming the mining waste piles, if appropriate protocols can be developed.

This research/demonstration program has been implemented as a sub-project of Project Silesia, a cooperative effort between the USEPA, USAID, the Polish national government and the Department of Ecology in Katowice, Upper Silesia, Poland (Pantuck et al., 1996). The reclamation of various mining wastes with municipal sewage sludge biosolids along with appropriate liming treatments has been proven effective in a variety of locations in the USA (Daniels et al., 1989; Sopper, 1992). The data and results presented in this paper summarize our efforts to come up with a viable and cost-effective technology for the revegetation of mining and smelter wastes with these two materials. Application of lime and sewage sludge to reclaim waste piles seemed to be an excellent alternative for topsoiling; however, our preliminary observations showed that implementing this method on smelter sites would require extensive research on waste geochemistry as well as selection of metal-tolerant plant cultivars.

## Experimental Methods

Over the spring and summer of 1994 we established two experiments at a Pb/Zn smelter site in the Katowice area to evaluate the potential for utilizing local sewage sludge and liming materials for revegetation. Two sites with a total area of 2 ha were selected at the Orzel Biały Smelter waste pile. The area selected was covered by two different zinc and lead smelter waste materials from (1) Doerschel furnace and (2) Welz process smelting technologies between 1950 and 1985. The area was completely barren of vegetation. In early 1994, bulk samples of the ungraded surface were collected and analyzed for total-S, pH and potential acidity by the hydrogen peroxide technique. Before the installation of experiments, over 160 point samples (from 0 - 5 and 20 - 25 cm) were collected on a 10 m grid and analyzed for pH, and total sulfur, zinc, cadmium, and lead. Water-soluble forms of Cd, Zn, Pb, Na and $SO_4^{2-}$ were also measured by extracting the material with water using a 1:2 (w/v) ratio. Electric conductance (EC) was also measured in these water extracts. All methods followed those of Page et al. (1982).

Before site grading and plot installation, the Welz material was pH 6.9 with a total-S content of 2.26%. We presume that the majority of this S was present as sulfate since the potential acidity by $H_2O_2$ was negligible. The Doerschel waste, on the other hand, was pH 3.6 with a total-S content of 10.7 %. The potential acidity of the Doerschel material was equivalent to 25 Mg of calcium carbonate per 1000 Mg material when titrated to pH 6.0, but generated a liming requirement of 75 Mg/1000 Mg when titrated to pH 7.0. We attributed this seemingly incongruous behavior to the dissolution of the smelter waste structure to some extent at increasing pH, releasing reduced S to solution from previously occluded forms. Based upon our assessment of these chemical properties and the local site conditions, the following reclamation treatments were implemented on 0.5 ha of each waste:

**1.** pH adjustment by application of 30 Mg/ha $CaCO_3$ and 15 Mg/ha CaO for the waste from the Doerschel furnace; and 30 Mg/ha of $CaCO_3$ and 1.5 Mg/ha of CaO for waste produced by the Welz process. This was then followed by application of sewage sludge at 0, 150, or 300 Mg/ha to 1/3 of each demonstration area.

**2.** Lime and sludge amendments were incorporated with a harrow and disc. Higher sludge rates were applied in split applications to ensure appropriate incorporation.

**3.** Seeding with metal- and salt-tolerant grasses was conducted in the fall of 1994. Grass cultivars were selected from short-term (90 day) germination/growth greenhouse tests as discussed later (Table 1).

It is important to note that our reason for adding lime to the Welz waste was to completely suppress water soluble metals, even though the initial pH was near neutral. Also, due to the fact that the ground-water quality below and around the waste piles has been seriously degraded by decades of deep mining and uncontrolled waste disposal, no effort was made in this study to document the "ground-water effects" of our treatments. Local and regional groundwater quality is an important issue to local authorities (Ochrona, 1993), and future studies in our program will assess the net water quality impacts of these stabilization approaches. However, the direct short-term human health risk from blowing metalliferous dust coupled with sediment losses to surface waters have been deemed so severe that surface revegetation and stabilization of the piles is of overwhelming importance to local environmental authorities.

In addition to the large demonstration plots on the smelter wastes described above, a replicated small plot experiment (30 m x 120 m overall size) in a randomized complete block design was installed on both Welz and Doerschel wastes to evaluate sludge loading rates, lime addition rates and grass species effects and interactions. The extreme spatial variability of chemical properties of the wastes, however, did not allow us to draw any conclusions based on classical statistical analysis. Therefore, spatial analysis was used to interpret the data as shown in this paper (see Fig. 1). At the end of each growing season, a monitoring program was conducted at each of the 10 m grid locations to measure above-ground biomass, metal content in plants, and changes of waste chemical properties including pH, metal solubility, and salinity.

In order to find an effective method for reducing metal mobility and toxicity in these smelter wastes, several laboratory experiments were conducted using different amounts of calcium oxide and calcium carbonate as waste amendments. Increasing amounts of CaO or $CaCO_3$ were added to 100 g samples of smelter waste materials which had been previously mixed with 60 g of sludge on a dry basis. Mixtures were equilibrated in a water slurry (1:2 ratio) by heating to 60 °C and stirring on a magnetic stirrer. Resulting solutions were centrifuged and analyzed for pH, EC, and soluble Cd, Zn and Pb (Page et al., 1982).

A greenhouse pot experiment with Welz material was performed to characterize the growth response of a number of grass and legume cultivars grown in a high metal and high salinity environment. Germination and biomass production were observed over a 90 day period. One subset of pots was spiked with 2% $Na_2SO_4$ to simulate observed field conditions typical of Welz and Doerschel materials, where we have observed EC as high as 10 dS/m (mmho/cm). A total of 20 different species were tested, with those shown in Table 1 selected for further use in the field trials.

## Results and Discussion

A number of the 20 grass cultivars that we tested in the pot experiment seem to be useful for revegetation purposes and exhibited different degrees of adaptation to chemical stress (Table 1). A mixture of the most acid/salt-tolerant species was used in the field trials discussed later. Additional detailed studies are ongoing on plant material adaptation at the field site.

Our survey of the raw waste deposits indicated that Doerschel and Welz material can contain extremely large amounts of Zn, Cd, and Pb (Table 2). The Doerschel material is much higher in these metals than Welz, and is also higher in EC, with salt levels that can dramatically inhibit plant growth (Bolt, 1991). Our demonstration plots and randomized complete block experiment were installed on both Welz and Doerschel wastes at this site; however, vegetation did not survive on the Doerschel material (Fig. 1), most likely due to the initial high salinity (16 dS/m) and metal toxicity related to water soluble Zn (1670 mg/kg) and Cd (108 mg/kg; Table 3).

Adverse physical properties of the Doerschel material, particularly high compaction and cementation, also contributed to total inhibition of plant growth. Lime and sludge at the rates used were not effective for establishment of vegetation; however, their incorporation reduced metal solubility which may decrease the potential of metal leaching from these piles. It should be emphasized that changes in pH and Cd solubility in both Doerschel and Welz materials were smaller than expected. Evidently, CaO was not effective for pH and metal solubility control in these materials, most likely due to limited solubility and/or occlusion with iron and other metal oxides that were present in solution at very high levels. Our laboratory experiments demonstrated that heavy rates of $CaCO_3$ did not result in substantial increase of pH or reduce Zn and Cd solubility; whereas CaO reduced metal mobility to ppb levels (Fig. 2). However, this effect may be temporary since a CaO buffering system can change with time into $CaCO_3$ via $CO_2$ sorption. This seems very likely, since the addition of CaO along with $CaCO_3$ to the field plots did not affect the initial pH or metal solubility to any great extent after

**Table 1. Resistance of different grass species to salinity and heavy metals**

| Grass species (cultivars) | Metal Tolerance | Salinity Tolerance |
|---|---|---|
| *Lolium perenne (Solen)* | +++ | +++ |
| *Lolium perenne ( Argona)* | +++ | +++ |
| *Lolium multiflorum (Telga)* | ++ | ++ |
| *Lolium multiflorum ( Koga)* | ++ | ++ |
| *Lolium x boucheanum Kunth. (Mega)* | ++ | ++ |
| *Poa pratensis (Alicja)* | +++ | - |
| *Festuca rubra (Atra)* | + | - |
| *Festuca arundinacea (SZD 492)* | ++ | + |
| *Festuca ovina (Sima)* | ++ | - |

**Table 2. Total metal content in waste materials sampled before treatment**

| Waste material | Zinc (g/kg) | | Cadmium (g/kg) | | Lead (g/kg) | |
|---|---|---|---|---|---|---|
| | average | range | average | range | average | range |
| Welz | 30.9 | 6.9-128 | 0.54 | 0.058-2.76 | 7.9 | 2.6-16.5 |
| Doerschel | 75.1 | 13.0-126 | 2.31 | 0.66-3.46 | 23.82 | 7.09-40.6 |

**Table 3. Chemical properties of waste material sampled before (1994) and after (1995) amendment with sewage sludge and lime**

| Waste material | Sampling time | Soluble zinc mg/kg | Soluble Cd mg/kg | Soluble Pb mg/kg | pH | EC dS/m |
|---|---|---|---|---|---|---|
| Welz | Before | 343 | 17.6 | 1.8 | 7.0 | 7.3 |
| | After | 279 | 17.7 | 1.1 | 7.2 | 3.5 |
| Doerschel | Before | 1670 | 108 | 5.4 | 5.8 | 16 |
| | After | 983 | 57.4 | 2.9 | 6.0 | 9.0 |

* values reported reflect averages of 80 samples of each material

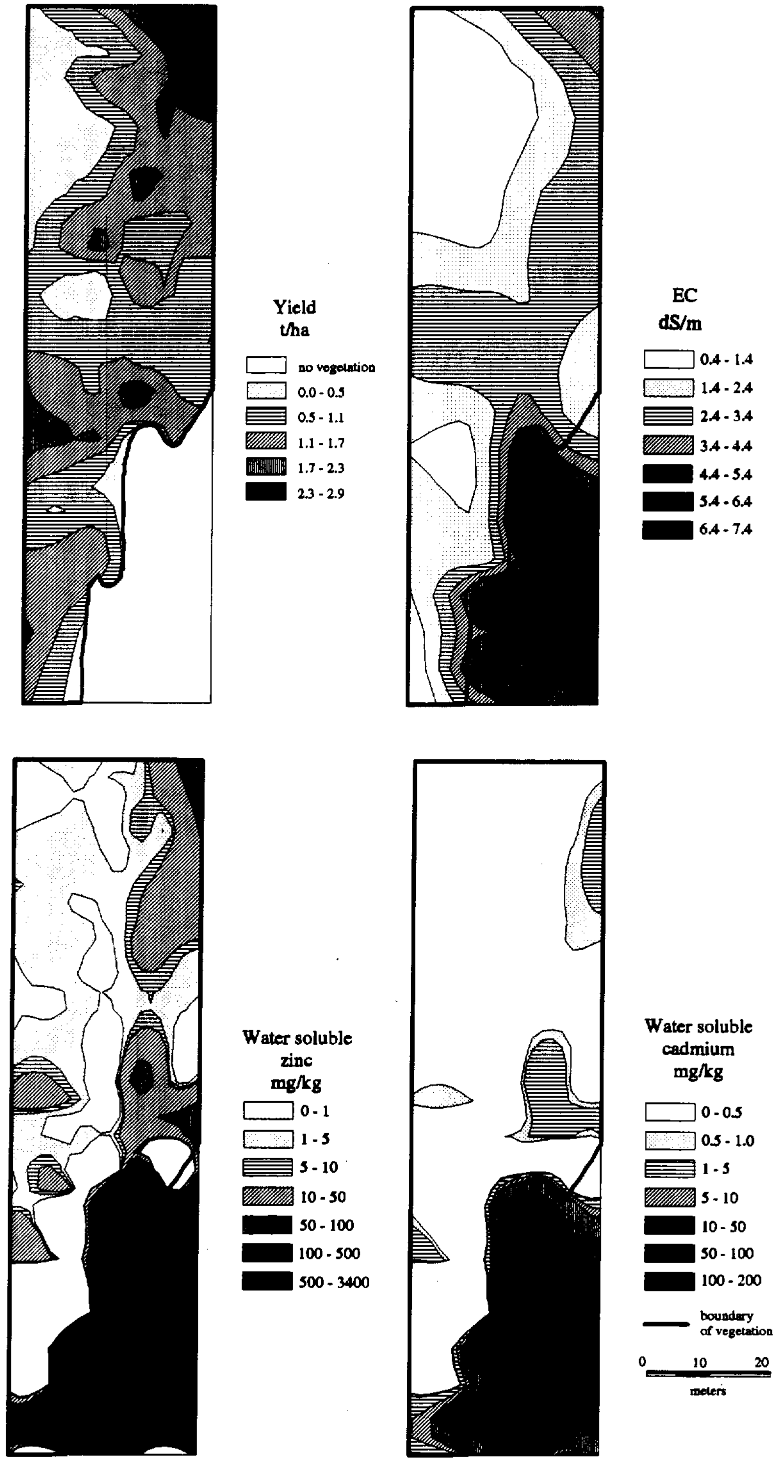


Figure 1. Standing biomass and soil chemical properties over the experimental area sampled in the late summer of 1995, one year after treatment and revegetation. Spatial plot is based on 160 point samples taken on a 10 m grid. The lower right hand corner of the block was dominated by Doerschel waste with associated high salinity and metal levels. The black line indicates the vegetated boundary. Note the strong association of metal levels with the vegetated boundary position. The reason for the low productivity in the upper left hand corner of the plots on Welz waste is not clear. However, this region was very low in soil sized (< 2 mm) materials and sludge incorporation was poor in this zone compared to the rest of the plot area.

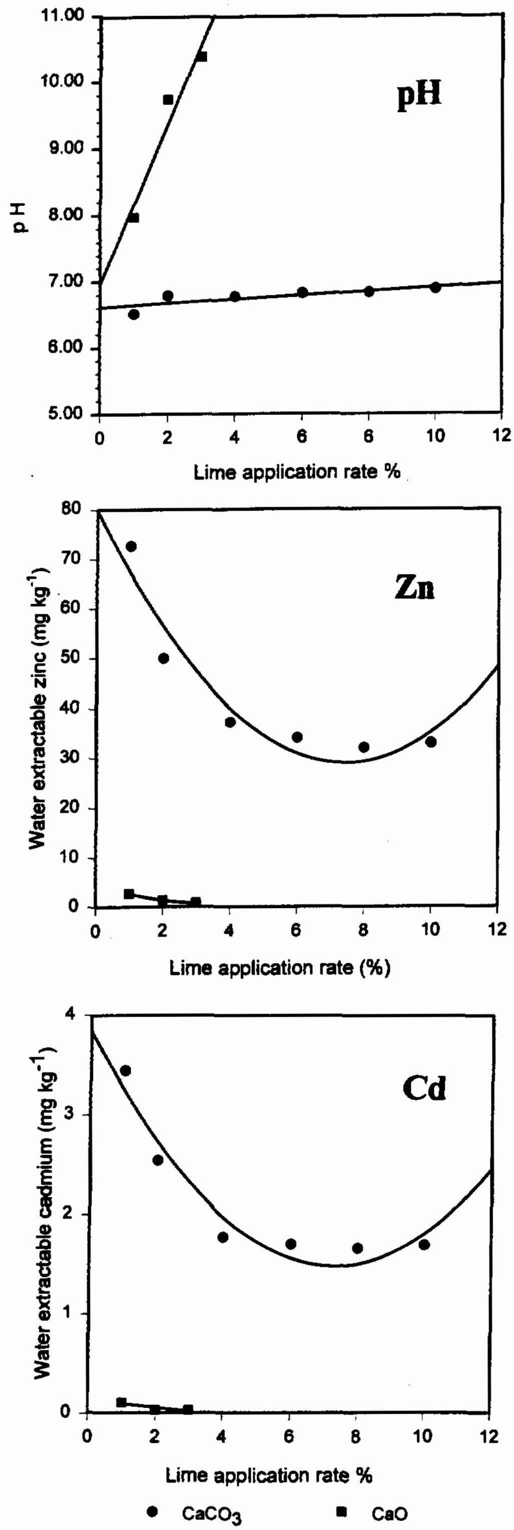


Figure 2. Influence of lime rate and type on pH and water soluble metal levels in Welz waste. The relationships point out the importance of driving the pH to levels > 7.0 to limit Zn and Cd solubility, even though the original pH was 6.6. The data also point out the relative inability of $CaCO_3$ alone to affect pH in this metalliferous system.

the first year (Table 3).

Vegetation (predominantly grasses; see Table 1) was successfully established on 85% of the Welz material plot (Fig. 1), even though it was high in water soluble Zn, Cd, and EC (Fig. 1). The spatial variability present in the waste piles under study provided a unique opportunity to characterize the extent of plant resistance to this harsh environment. It seems obvious from our spatial analysis that soluble Zn, Cd, and high salinity are the most limiting factors controlling the effectiveness of revegetating these smelter wastes (Fig. 1). However, it is also obvious that these elements co-vary together and we cannot isolate one as being singularly phytotoxic. This analysis does enable us to conclude that the grass cultivars used can adapt to the relatively harmful conditions seen in the treated Welz material (Table 4).

The Doerschel waste area was retreated in 1995 with a 15 cm cap of waste lime ($CaO + CaCO_3$), which subsequently received 300 Mg/ha municipal sludge. The sludge was incorporated (by harrow/disc) into the lime cap and seeded with the same tolerant seed mix used in 1994. This treatment resulted in 75 to 80% ground cover by the spring of 1996, with little evidence of metal toxicity in the vegetation. On-site soil evaluation indicated that the roots penetrated to the lime/waste interface, but no more than 2 cm into the underlying Doerschel material. Thus, the ability of the treatment to sustain the vegetative community through summer droughts will need to be evaluated over time. The Welz waste area was similarly evaluated in 1996, and continued to support vigorous herbaceous vegetation, including legumes. We also noted a number of perennial herbaceous and woody species invading the plots from the surrounding area, supporting our hypothesis that the chemistry of these materials has been sufficiently stabilized to support long term plant growth. Plant roots penetrated into the treated Welz materials to a depth of 10 to 20 cm.

## Conclusions

The success of any stabilization/revegetation effort such as this needs to be evaluated over multiple seasons. However, we are encouraged by the persistence of vegetation on these wastes over multiple seasons. Based upon our experience with these studies, we recommend a one-time application of lime and stabilized sewage sludge that has undergone appropriate pathogen reduction and meets regulatory heavy metal loading limits. The rates of lime and sludge utilized should be calculated after a detailed survey of the particular waste's chemical properties. For extremely toxic waste, such as Doerschel material, heavy rates of lime are recommended to ensure successful, permanent revegetation. We will need several more years to evaluate the full results of our restoration trials in the Katowice area before finalizing sludge utilization guidelines that have been developed (Pantuck et al., 1996). However, it is clear that locally produced sewage sludge biosolids can be effectively used in combination with heavy liming at many mining waste piles in this region to drastically reduce wind and water erosion losses to surrounding communities. This option has proven to be much cheaper than thick topsoiling, or other advanced engineering approaches such as bulk processing or encapsulating the entire fill. Finally, this approach can simultaneously solve the current and impending sludge management problems faced by this region. The effects of this procedure on ground-water quality were not evaluated in this study, and the potential for nitrate contamination at these loading rates cannot be overlooked.

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**Table 4. Maximum observed levels of chemical properties within vegetated areas**

| Zinc mg/kg | | Cadmium mg/kg | | Lead mg/kg | | Soluble Na mg/kg | Sulfates (mg/kg) | EC dS/m |
|---|---|---|---|---|---|---|---|---|
| total | sol.. | total | sol. | total | sol. | | | |
| 100.000 | 1.000 | 1700 | 55 | 11000 | 3.7 | 1600 | 20000 | 5.4 |

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