EFFECTS OF PHOSPHOGYPSUM AND MAGNESIUM CHLORIDE AMENDMENTS ON ABANDONED BENTONITE MINE SPOILS

by

S.C. Smith and D.J. Dollhopf

ABSTRACT. Reclamation of abandoned sodic bentonite mine spoils is difficult due to elevated salinity and sodicity, and high smectite clay content. These spoils readily disperse upon wetting resulting in minimal water infiltration and the formation of impermeable surface crusts. Chemical amendments have recently been shown to be effective in ameliorating the adverse physicochemical properties inherent to these abandoned spoils. Experimental field plots were implemented to investigate the effectiveness of phosphogypsum and magnesium chloride brine as spoil amendments. These materials are low cost industrial by-products.

Analysis of amendment chemical constituents indicated that the phosphogypsum was 82.1% CaSO₄·2H₂O and the magnesium chloride brine was 40.8% MgCl₂. The phosphogypsum was enriched in silver, cadmium, and selenium. However, amendment incorporation results in approximately 110:1 dilution which should prevent trace element accumulations.

After two growing seasons, application of these amendments resulted in reduced SAR and saturation percentage, and improved water infiltration. Improvements in these minesoil physicochemical parameters indicates that a more desirable plant growth medium is being developed.

Additional Key Words: Bentonite spoil reclamation, physicochemical properties, chemical amendments, trace elements, industrial by-products.

Introduction

Swelling capacity and thixotropic properties make bentonite a valued industrial mineral. These properties are enhanced when sodium is the dominant adsorbed cation. Because of the wide variety of commercial uses, bentonite has been mined for many years in the Northern Great Plains. The tri-state region of Montana, Wyoming, and South Dakota contains approximately 90% of the world's economically minable deposits of high-grade sodium bentonite (Romo 1981).

Prior to the enactment of reclamation laws governing bentonite mining in the early 1970's, mined areas were left totally unreclaimed. An estimated 16,000 to 26,000 hectares of abandoned bentonite spoils are the result of pre-regulation mining activities (Smith et al. 1985). The clayey, saline-sodic nature of these spoils create adverse physicochemical properties. When the spoil receives precipitation, the combination of smectite clay mineralogy and high SAR (sodium adsorption ratio) result in spoil swell from clay dispersion. Mine spoil swelling processes substantially reduce hydraulic conductivity and permeability, and result in the formation of surface crusts that restrict seedling emergence. Due to these adverse conditions, invasion of native plant species is precluded and revegetation is difficult.

Bentonite reclamation technology was limited even into the 1980's. Sieg et al. (1983) found that topsoiling alone was not adequate for successful reclamation of abandoned bentonite spoils. Encouraging results have been reported using organic amendments. Wood residue amendment is known to improve vegetative production on bentonite spoils (Schuman and Sedbrook...
Dollhopf et al. (1988) reported increases in long-term forage production using manure as an amendment. However, the ability of organic amendments to ameliorate long-term spoil physicochemical problems is uncertain. Anselmi (1986) reported that wood residue amendment did not alleviate the sodium problem in bentonite spoils.

Chemical amendments which supply calcium ions have been utilized for reclamation of sodic mine spoils. Calcium ions are strongly adsorbed and replace sodium on cation exchange sites. Through this mechanism, clay dispersion is reduced and spoil physicochemical properties are improved. Chemical amendment use significantly increases reclamation costs. Therefore, the identification of effective and low cost amendments is needed.

**Amendments**

**Phosphogypsum**

Phosphogypsum is a by-product of the phosphate fertilizer industry. Phosphate ore containing calcium is processed with sulfuric acid (H₂SO₄). Gypsum (CaSO₄·2H₂O) is precipitated as a silt sized (<0.02-0.05mm) waste product. Phosphogypsum consists of the gypsum tailings material (80-99% CaSO₄·2H₂O), mineral impurities, and less than 1% phosphate (P₂O₅) (Keren and Shainberg 1981). Thousands of tons are produced annually in the United States with no apparent market.

In semi-arid environments, dissolution of agricultural (mined) gypsum is slow when applied to non-irrigated sodic mine soils. Because of the silt particle size, phosphogypsum has much more surface area than agricultural gypsum at a given fragment size (Keren and Shainberg 1981). These researchers found that due to the increased surface area, phosphogypsum has approximately ten times the dissolution rate as agricultural gypsum. Increased dissolution enables phosphogypsum to supply exchangeable calcium at a much faster rate.

Incorporation of phosphogypsum into the spoil profile can result in improved physicochemical properties. Gal et al. (1984) reported that phosphogypsum application reduced clay dispersion at the soil surface helping to prevent crust formation. Kazman et al. (1983) found that incorporated phosphogypsum prevented the sharp reduction in infiltration as the soil profile became wet.

**Magnesium Chloride Brine**

Magnesium chloride brine is produced as a by-product at table salt (NaCl₂) evaporation facilities. The brine consists of 35 to 45% MgCl₂, with minimal amounts of calcium, sodium, potassium, nitrate, and sulfate occurring as impurities.

As divalent alkaline earth metals, magnesium and calcium possess similar properties. Richards (1969) classified calcium and magnesium as similar ions important in soil structure development. Magnesium effectively replaces sodium from cation exchange sites (Arora and Coleman 1979).

Calcium chloride is a well known, effective amendment for sodic soils. The high solubility of calcium chloride (745 g/L) has proven to be the key to its effectiveness. Magnesium chloride solubility (542 g/L) is also very high compared to agricultural gypsum (2.4 g/L).

Similar properties give magnesium chloride the potential to be as effective as calcium chloride in sodic soil reclamation. However, the only known field research using magnesium chloride as a soil amendment occurred in the Soviet Union. In this study, Papinyan (1980) reported significant soil ESP (exchangeable sodium percentage) reductions and improved soil-water relationships when magnesium chloride was used to amend sodic soil.

Plant growth is thought to be adversely affected by a low Ca²⁺/Mg²⁺ ratio in the soil. Bohn et al. (1985) stated that high magnesium concentration may repress calcium uptake. Application of magnesium chloride brine as an amendment will elevate magnesium levels. Although there is potential for plant growth problems, Simson et al. (1979) found that satisfactory plant growth could be maintained between Ca²⁺/Mg²⁺ ratios of 0.8 to 5.0.

**Materials and Methods**

In May of 1986, field plots were implemented near Belle Fourche, South Dakota on abandoned sodic bentonite mine spoils. Test plots were located directly adjacent to a 1980 bentonite field study (Dollhopf and Bauman 1981). The spoil material consisted predominantly of the Belle Fourche Shale. Precipitation in the area averages 36.7 cm/yr. Dominant plant species on undisturbed native rangeland are big sagebrush (Artemisia tridentata) and western wheatgrass.
(Agropyron smithii). Bentonite mining in the area began in the early 1900's and is currently active.

Representative samples of each chemical amendment were taken prior to application for analysis of purity and total trace element concentrations by method 3050 (EPA 1982). Spoil core samples were taken before plot implementation to help characterize the site.

Unamended Mine Spoil Characterization

The test plots were located in an area of previously leveled spoil which was found to be homogeneous in an earlier study (Dollhopf and Bauman 1981). Insufficient space in the leveled area prevented new control plots from being implemented. Therefore, values for unamended spoil physicochemical properties were developed using all available data from the site. These data include SAR, EC, and saturation percentage values from several data sets obtained over a 7 year period.

Plot Implementation and Sampling Procedures

Test plot implementation began with chisel plowing of the plot area. Six, 5 x 15 m plots were staked in a block design with three replications of phosphogypsum (40.4 mt/ha) and three replications of magnesium chloride brine (36.2 mt/ha). Amendments were manually applied followed by rototilling for incorporation. Test plots were broadcast seeded, and mulched. Application rates for the chemical amendments were stoichiometrically calculated to potentially reduce SAR by 20 units (Smith 1988). This reclamation goal, if attained, would remove these spoils from the sodic classification.

Two, 0 to 35 cm core samples were taken from each plot in September of 1986 (4 months following plot implementation) and in July of 1987 (14 months following plot implementation). For each plot, core samples were divided into four depth increments and composited. Depth increments were 0 to 5 cm, 5 to 10 cm, 10 to 20 cm, and 20 to 35 cm.

In the laboratory, saturation percentage of core samples was determined by methods 26 and 27b (Richards 1969). Saturated paste extracts were evacuated from each sample for determination of SAR and EC (electrical conductivity).

In July of 1987, infiltration rates were measured on the phosphogypsum and magnesium chloride brine treated plots, and at 3 random locations on unamended spoil directly adjacent to each treatment replication. An infiltrometer built from construction plans presented in Meeuwig (1971) was used to simulate rainfall at the rate of 12 cm/hr. Runoff was measured over 5 minute intervals and values were used to determine infiltration rates.

To provide statistical summarization and comparison, analysis of variance (ANOVA) was conducted on all data sets. Least significant difference (LSD) at a 95% confidence interval was calculated for mean values in each data set. Coefficients from LSD calculations are included in Tables 2-4.

Results and Discussion

Amendment Chemical Characteristics

Results from amendment analyses indicated that the applied phosphogypsum was 82.1% CaSO₄·2H₂O. The magnesium chloride brine contained 40.8% MgCl₂. In the phosphogypsum amendment, total silver (Ag) concentration was 15% greater than the suspected phytotoxic level (EPA 1987b). Total cadmium (Cd) and selenium (Se) concentrations were enriched above expected background levels in soil (Kabata-Pendias and Pendias 1984, Shacklette and Boerngen 1984). Total concentrations of the other analyzed trace elements were within the normal range for soils (Table 1). No enrichment of trace elements was detected in the magnesium chloride brine.

Assuming that 1 acre-ft of spoil weighs 4 million pounds, incorporation (35 cm) of the phosphogypsum amendment results in dilution of 40.4 metric tons (mt) into 4480 (mt) of spoil within 1 hectare. This represents a dilution ratio of approximately 110:1. Although several trace elements were enriched in the phosphogypsum, amendment dilution minimizes the potential for plant growth problems.

Radium 226 occurs in much of the phosphate ore from the Western United States. Phosphogypsum tailings produced in Idaho and Utah are reported to have concentrations of radium 226 exceeding the U.S. EPA suspect level of 5 picocuries/gram (Range Inventory and Analysis 1986). In a Wyoming study, 12 inch incorporation of phosphogypsum amendment (35.5 mt/ha) with an average of 26 picocuries/gram radium 226, resulted in no significant increase in radium 226 levels compared to background levels (Range Inventory and Analysis 1986).
Table 1. Trace element total concentrations in phosphogypsum and magnesium chloride brine amendments.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>BACKGROUND PHOSPHOGYPSUM</th>
<th>PHYTOTOXIC MAGNESIUM CHLORIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>.03-.18 g</td>
<td>0.36 g</td>
</tr>
<tr>
<td>Aluminum</td>
<td>57,000 i</td>
<td>1.2</td>
</tr>
<tr>
<td>Arsenic</td>
<td>3.6-8.6 d</td>
<td>1.4</td>
</tr>
<tr>
<td>Barium</td>
<td>265-835 c</td>
<td>7.3</td>
</tr>
<tr>
<td>Beryllium</td>
<td>1.6 c</td>
<td>0.22</td>
</tr>
<tr>
<td>Cadmium</td>
<td>.07-1.1 c</td>
<td>10.0</td>
</tr>
<tr>
<td>Cobalt</td>
<td>6.2 c</td>
<td>0.004</td>
</tr>
<tr>
<td>Chromium</td>
<td>20-65 d</td>
<td>0.08</td>
</tr>
<tr>
<td>Copper</td>
<td>10-50 b</td>
<td>0.8</td>
</tr>
<tr>
<td>Iron</td>
<td>27,500 c</td>
<td>28.8</td>
</tr>
<tr>
<td>Mercury</td>
<td>.04-.26 d</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Manganese</td>
<td>260-840 d</td>
<td>3.3</td>
</tr>
<tr>
<td>Nickel</td>
<td>10 c</td>
<td>0.06</td>
</tr>
<tr>
<td>Lead</td>
<td>17-26 d</td>
<td>4.4</td>
</tr>
<tr>
<td>Antimony</td>
<td>10 f</td>
<td>1.0</td>
</tr>
<tr>
<td>Selenium</td>
<td>2.2-5.5 d</td>
<td>5.0</td>
</tr>
<tr>
<td>Tin</td>
<td>6-1.7 d</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Thallium</td>
<td>0.02-2.8 h</td>
<td>.1</td>
</tr>
<tr>
<td>Vanadium</td>
<td>58 d</td>
<td>0.9</td>
</tr>
<tr>
<td>Zinc</td>
<td>34-93.5 d</td>
<td>0.9</td>
</tr>
</tbody>
</table>

1 - Concentrations given in ppm on dry weight basis.
2 - Background level for soils.
3 - Sources are: a is EPA (1987a); b is EPA (1987b); c is Kabata-Pendas and Pendas (1984); d is Shacklette and Boerngen (1984); e is Kovalskiy (1974); f is Kabata-Pendas (1979); g is Smith and Carson (1977a); h is Smith and Carson (1977b); and i is Tidball and Severson (1975).

Unamended Mine Spoil Physicochemical Characteristics

Representative unamended spoil SAR and EC across the research site were determined to be 33.8 and 8.0 Ds/m, respectively. The representative value for unamended spoil saturation percentage was 127. The preceding mean values were developed using data sets from 1980 pre-amendment sampling, 1986 sampling of the 1980 control plots, and pre-amendment sampling for this study.

Minesoil Sodium Adsorption Ratio (SAR)

Four months (1986) following amendment application, the SAR on magnesium chloride plots was significantly less than on spoil or phosphogypsum plots at 0 to 5 cm (Table 2). Little change in SAR was noted on amended plots over the 10 to 35 cm depth at this time. The SAR reduction on magnesium chloride plots suggests that this amendment is highly effective within 4 months following application.

Minesoil Electrical Conductivity (EC)

Fourteen months (1987) following amendment application, both magnesium chloride and phosphogypsum treated plots (0-5 cm) were significantly less in SAR compared to unamended spoil (Table 2). The SAR reduction of 9.3 units on phosphogypsum plots (0-5 cm) corresponds to 46% of the SAR reduction goal. On magnesium chloride plots, the reduction of 12.5 SAR units indicates 62% effectiveness. Over the 5 to 35 cm depth, SAR reductions were also detected on treated plots.

Minesoil SAR improvements were most apparent near the surface. As physical properties such as structure and permeability improve as a function of reduced SAR, more water will infiltrate into the profile. Progressively, minesoil physicochemical improvements should occur at depth as a function of increased infiltration.

Application of either phosphogypsum or magnesium chloride brine increased minesoil salinity levels compared to the unamended spoil EC value of 8.0
dS/m. Four months (1986) following amendment application, EC values from saturated paste extracts were significantly greater on magnesium chloride brine treated plots (0-20 cm) compared to unamended spoil (Table 3). At the 0 to 5 cm depth, salinity increased by 39% on phosphogypsum plots and 112% on magnesium chloride plots.

Fourteen months (1987) following amendment application, EC values on magnesium chloride plots were significantly greater than unamended spoil over the entire amended depth (Table 3). At the 0 to 5 cm depth, EC was 57% greater on magnesium chloride plots compared to phosphogypsum plots.

Table 3. Minesoil electrical conductivity (EC) values at the Belle Fourche site.

<table>
<thead>
<tr>
<th>YEAR</th>
<th>TREATMENT</th>
<th>0-5cm</th>
<th>5-10cm</th>
<th>10-20cm</th>
<th>20-35cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>Phos-gyp</td>
<td>11.1</td>
<td>10.9</td>
<td>9.5</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>MgCl₂</td>
<td>17.0</td>
<td>19.1</td>
<td>12.4</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td>Spoil</td>
<td>8.0</td>
<td>8.0</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>1987</td>
<td>Phos-gyp</td>
<td>10.1</td>
<td>11.6</td>
<td>11.6</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>MgCl₂</td>
<td>15.9</td>
<td>14.0</td>
<td>12.8</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>Spoil</td>
<td>8.0</td>
<td>8.0</td>
<td>8.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>

1 - Values from treated plots represent the mean of 3 replications. Spoil values represent the overall mean from 3 data sets.
2 - Means followed by the same letter in the same column indicate no significant difference (P=0.05).

Over the remainder of the amended profile, magnesium chloride plots had EC values consistently greater than phosphogypsum plots, but to a lesser degree than at 0-5 cm. The range in EC on magnesium chloride plots indicated that after 14 months salinity remained 60 to 99% higher than pre-amendment levels.

Although high salinity inhibits water uptake by plants, there was a net improvement in the plant growth medium due to improved minesoil physicochemical properties.

Minesoil Saturation Percentage

Saturation percentage determinations were performed on core samples taken in the summer of 1987 to relate improvements in minesoil SAR to physical properties. Saturation percentage gives an indication of the severity of soil structure breakdown due to clay mineral dispersion. In a dispersed condition, pore space is reduced or eliminated decreasing water transmission through the minesoil. Reduced values for saturation percentage correspond with improved minesoil physical properties.

Saturation percentage was significantly less on both phosphogypsum and magnesium chloride brine treated plots (0-5 cm) compared to unamended spoil (Table 4). In comparing amended test plots, saturation percentage was significantly less on magnesium chloride brine treated plots (0-5 cm) at 73, compared to 103 on phosphogypsum treated plots. These values indicate a 42% reduction on magnesium chloride plots and a 19% reduction on phosphogypsum plots over 0 to 5 cm. Saturation percentage was also reduced throughout the 5-35 cm depth for both treatments suggesting that the severity of swelling processes had been decreased.

Table 4. Summer, 1987 minesoil saturation percentage at the Belle Fourche site.

<table>
<thead>
<tr>
<th>TREATMENT</th>
<th>0-5</th>
<th>5-10</th>
<th>10-20</th>
<th>20-35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphogypsum</td>
<td>103 b</td>
<td>111 b</td>
<td>128 b</td>
<td>122 a</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>73 a</td>
<td>80 a</td>
<td>90 a</td>
<td>95 a</td>
</tr>
<tr>
<td>Spoil</td>
<td>127 c</td>
<td>127 b</td>
<td>127 b</td>
<td>127 a</td>
</tr>
</tbody>
</table>

1 - Values from treated plots represent the mean of 3 replications. Spoil values represent the overall mean from 2 data sets.
2 - Means followed by the same letter in the same column indicate no significant difference (P=0.05).

Minesoil Infiltration Rates

The infiltration rate study was conducted to determine if the applied amendments increased infiltration into the minesoil profile. Sodic mine spoils typically allow near normal infiltration initially, but exhibit dramatic infiltration rate reductions within a short time due to soil pore blockage from clay dispersion.

Results from the infiltration rate study indicate that infiltration rates improved on amended test plots (Figure 1). The 5 to 10, and especially the 10 to 15 minute infiltration rates clearly demonstrate the effects of the amendments. By 10 to 15 minutes, minimal infiltration was occurring on unamended spoil. Nearly all precipitation was being converted to runoff. Erosion potential increased and moisture needed in the root zone was lost. Over the same time period, substantial infiltration was occurring on the amended test plots. After 30 minutes of simulated rainfall, amended test plots maintained moderate (2-6 cm/hr) infiltration rates.
On unamended spoil, the infiltration rate dropped to 0.1 cm/hr.

Results from the infiltration rate study indicate that the combination of chisel plowing, chemical amendments, seeding, and straw mulch improved surface water infiltration into the minesoil. It is likely that a majority of the improvement in infiltration is due to the application of the chemical amendments. The effects of plowing and mulch may be minimized after 14 months due to minesoil shrink-swell processes and mulch decomposition. Reduced saturation percentages on amended plots suggest that water movement through the minesoil profile should increase.

**Summary**

Application of either phosphogypsum (40.4 mt/ha) or magnesium chloride brine (36.2 mt/ha) in combination with chisel plowing, seeding, and mulch resulted in reduction of SAR and saturation percentage, particularly near the surface. Four months following amendment application, mean SAR on magnesium chloride brine treated plots (0-5 cm) declined significantly from an unamended spoil SAR of 33.8, to 20.4.

Fourteen months following amendment application, mean SAR (0-5 cm) was 21.3 on magnesium chloride treated plots and 24.5 on phosphogypsum treated plots. These SAR values were both significantly less than unamended spoil. Saturation percentage (0-5 cm) declined from an unamended spoil value of 127, to 73 and 103 on magnesium chloride and phosphogypsum plots, respectively. These results suggest that application of either amendment will result in SAR and saturation percentage reductions. However, these reductions occur more rapidly with the magnesium chloride brine amendment.

An initial rise in EC near the surface occurred following application of either amendment. Four months following amendment application, EC (0-10 cm) increased an average of 37% on phosphogypsum treated plots and 125% on magnesium chloride treated plots. After two growing seasons (14 months), EC appeared to be declining near the amended surface. However, limited data makes this trend difficult to confirm.

Minesoil infiltration rates were significantly increased by the application of either amendment. After 30 minutes of simulated rainfall, amended test plots maintained moderate (2-6 cm/hr) infiltration rates. Over the same time period, the infiltration rate on unamended spoil dropped to .1 cm/hr.

---

Figure 1. Minesoil infiltration rates over time at the Belle Fourche site.

![Figure 1. Minesoil infiltration rates over time at the Belle Fourche site.](image-url)
The phosphogypsum amendment was enriched above background levels in cadmium and selenium, and contained silver at concentrations slightly above suspected phytotoxic levels. However, because of dilution by amendment incorporation, trace element accumulations are unlikely. No enrichments in trace elements were detected in the magnesium chloride brine. As industrial by-products, both phosphogypsum and magnesium chloride brine create disposal problems at processing facilities. Use of these materials to reclaim disturbed sites produces a two-fold reclamation success. As waste products, these amendments are considerably less expensive than their counterparts, mined gypsum and calcium chloride.

Abandoned sodium bentonite mine spoils are a difficult reclamation challenge requiring amendments that are effective, yet cost feasible. Phosphogypsum or magnesium chloride brine application to this mine soil decreased the SAR and saturation percentage, while improving infiltration rates. Fourteen months following plot implementation, the plant growth medium had been improved allowing vegetation to be well established.

Literature Cited


