

Extractable Heavy Metals in Phosphogypsum

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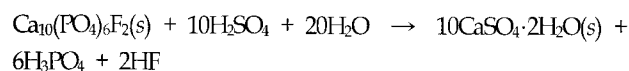
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ABSTRACT : In addition to supplying the essential elements, Ca and S, phosphogypsum can have profound effects on both the physical and chemical properties of certain soils. However, no widespread use of by-product phosphogypsum will be made unless such uses pose no threat to the public health and soil contamination. In this study, the extractability of As, Cd, Cu, and Pb with water and DTPA solution from phosphogypsum samples of pH 3, 5, and 7 were investigated to estimate the availability of those metals. Contents of water extractable metals in phosphogypsum were less than 5 mg/kg for all the heavy metals investigated. The extractability of metals in DTPA solution was not quite different but a little higher in comparison to the water extraction. And the extractability was decreased as the pH of phosphogypsum increased. In the phosphogypsum of pH 7, amounts of water extractable metals were nearly zero. There was no significant difference in the amount of extractable metals during the extraction period of 5 weeks. The length of extraction time did not affect heavy metal extractability. Therefore there may be small fractions of easily soluble or extractable forms of metals in the phosphogypsum and most of the metals would be present in very insoluble forms. These results suggest that the application of phosphogypsum at appropriate rates on agricultural lands appears of no concern in terms of hazardous element contamination in soil.

Key words: phosphogypsum, heavy metal, As, Cd, Cu, Pb

INTRODUCTION

The mineral fluoroapatite is treated with sulfuric acid to produce phosphoric acid in the following wet-process acidulation:



The phosphoric acid is used to manufacture high-analysis P fertilizers, while the by-product gypsum is collected as a waste product. The stoichiometry and masses involved in the reaction result in production of hydrated CaSO_4 in amounts equal to 1.0~1.5 times the mass of fluoroapatite reacted. This fine-grained, high-purity material, termed phosphogypsum, is produced in large quantities in worldwide, and presents a serious disposal problem¹⁾.

Phosphogypsum is typically 85~95% gypsum; the major impurity is residual quartz sand (SiO_2), which may range from 3~17%. Residual P and F may make up 0.1~1.0% of phosphogypsum as well.

The increased environmental awareness of the past decades has placed a greater emphasis on waste recycling, and enormous efforts are being made to spend phosphogypsum in established markets such as cement additives, wallboard manufacture, and traditional agricultural uses^{1,2)}. Agronomic use of phosphogypsum is highly desirable from the point of view of recycling by-product and eliminating the need for stockpiling. So far phosphogypsum has been known as a very effective soil amendment in the amelioration of acidic subsoil and dispersive soils. Shainberg et al. and Sumner have been reviewed the use of phosphogypsum to ameliorate subsoil acidity of soils around the world^{3,4)}. Lime is totally ineffective in supplying Ca to subsurface soils due to its insolubility in limed top soils. Gypsum, however, continually dissolves to move Ca^{2+} with percolating water into subsoil horizons.

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Table 1. Total analysis of phosphogypsum used in this study.

pH	CaSO ₄ · 2H ₂ O	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	As	Cd	Cu	Pb
	%				mg/kg				
3.0	93	3.5	0.9	0.8	44	0.7	1.4	2.6	4.7

In a long-term experiments with gypsum incorporated into the top soil, exchangeable Ca and SO₄ were higher down the soil profile in the gypsum than in the control treatment and complementary reduction in exchangeable Al was observed⁹. Gypsum has been used for remediation of sodic soils for some time, acting largely to replace exchangeable Na with Ca; it also has a marked effect on non-sodic, dispersive soils by supply electrolyte to the soil solution. Results summarized by Shainberg et al. indicate that gypsum applied on the soil surface prior to rainfall significantly increases infiltration rate, total infiltrated water, and reduces soil erosion³. Several observations have suggested surface-applied gypsum may be effective in reducing crust strength and increasing emergence on dispersive soils^{6,7}.

However, potential environmental concerns are an important consideration in suggesting any material as a soil amendment, particularly a waste or by-product such as phosphogypsum⁸. While the major constituents (Ca and SO₄) are not likely to be considered environmentally damaging in soils and ground or surface waters, phosphogypsum may contains free acidity, radioactive elements and heavy metals, carried over from the primary processing.

When phosphogypsum is considered as a soil amendment, contamination of soils with heavy metals and other trace elements is possible, and such possibility of hazardous element contamination has hindered agricultural use of the material. Considering that the total level of hazardous elements in phosphogypsum is nearly the same level of natural soil materials, applications of the material at appropriate rates on agricultural land appears of no concern in terms of contamination of soils with hazardous elements⁹. However, there are still few researches in relation to the availability of hazardous elements of phosphogypsum in soils.

In this study, the extractability of heavy metals with water and DTPA solution from phosphogypsum were investigated under laboratory conditions to estimate the availability of those hazardous elements.

MATERIALS AND METHODS

Extraction experiments

Phosphogypsum used in this experiment was obtained from Namhae Chemical Co., and the general properties were described in Table 1. pH of the phosphogypsum was 3.0 and additional phosphogypsum samples of pH 5.0 and 7.0 were prepared by addition of Ca(OH)₂. The pH-adjusted phosphogypsum samples were stored for 1 month to stabilize pH and other chemical characteristics at moisture content of 20% under laboratory conditions. The phosphogypsum samples were dried at 50°C before the experiment.

Heavy metals including As, Cd, Cu, and Pb were extracted with deionized water and 0.005 M DTPA (Diethylene triamine pentaacetic acid) solution (pH 7.3) containing 0.01 M CaCl₂ and 0.1 M triethanolamine¹⁰. Ten g of phosphogypsum were mixed with 25 mL of deionized water or 0.005 M DTPA solution in 50 mL plastic centrifuge tubes. The mixtures were shaken at 200 rpm on a reciprocating shaker for 5 weeks at 20±2°C. Heavy metals extracted were measured several times during the extraction period. The suspensions were centrifuged at 8000×g for 10 min and filtered through 0.45 μm membrane filter. Heavy metals in the filtrate were analyzed as described below.

Analytical methods

pH was determined using 1:5 water suspensions with a combination glass electrode. Elemental composition of phosphogypsum was determined after digestion with strong acids (HNO₃ + HF + HCl) using a Varian Liberty Series II (Mulgrave, Australia) inductively coupled argon plasma emission spectrometry (ICP-ES). Heavy metals extracted in water and DTPA solution were also measured using ICP-ES.

RESULTS AND DISCUSSION

pH of phosphogypsum is generally in the range of 1.8 ~5.5 depending of the storage conditions. Free acids contained in the pore fluids of phosphogypsum are the reason for the lower pH. Although this low pH is considered as one of the limiting factors in recycling of phosphogypsum as a soil amendment, the acidity of phosphogypsum is not strongly buffered. Considering the strong buffering capacity

of natural soil systems, acidification in soils amended with phosphogypsum is expected not to be very significant⁹.

However, to eliminate public or agronomic concerns about the low pH of phosphogypsum, partial or complete neutralization of the acidity of phosphogypsum may be necessary before using it as a soil amendment. Therefore, pH of the phosphogypsum was adjusted to 5 and 7 using solid $\text{Ca}(\text{OH})_2$ for the heavy metal extraction study, and only 26 and 78 mmol of OH^- were required for 1 kg of phosphogypsum. In addition to the neutralization of acidity, this pH adjustment may alter and stabilize the chemical characteristics of heavy metal compounds in the phosphogypsum.

Since contamination levels of heavy metals in rock phosphate are quite different depending on the mining sites, the heavy metal contents in phosphogypsum are also dependent on the rock phosphates used in acidulation process. The phosphogypsum used in this experiment was produced using rock phosphate imported from China. Heavy metal contents in the phosphogypsum were quite low as shown in Table 1. Comparing to the average content of heavy metals in upland soils¹¹, Pb content in the phosphogypsum was higher than the average content in upland soils, and other metal contents were in the range of those contents in upland soils. Average metal contents in phosphogypsum of Namhae Chemical Co. were much lower than those in composts of municipal sewage sludge¹² and the phosphogypsum produced from Florida rock phosphate, containing 2~8, 3~6, 2~12 and 0.5~2 mg/kg of As, Cd, Pb and Se, respectively¹³.

Although heavy metal contents are quite low, potential environmental concerns are a particularly important consideration in suggesting a waste or by-product such as phosphogypsum as a soil amendment. In addition to the total contents, availability of the metals after application of phosphogypsum in soil should be further considered. Transport of heavy metals in phosphogypsum to plants or water systems around the application sites is directly related to the availability of those metals in soils rather than the total amount. To evaluate the availability of heavy metals in phosphogypsum, extractability of the metals in water and DIPA solution were investigated under laboratory conditions in this study. Heavy metal extractabilities in deionized water for the phosphogypsum samples of different pHs were presented in Fig. 1.

Extractable contents were less than 5 mg/kg for all the heavy metals investigated, and the extractability was decrea-

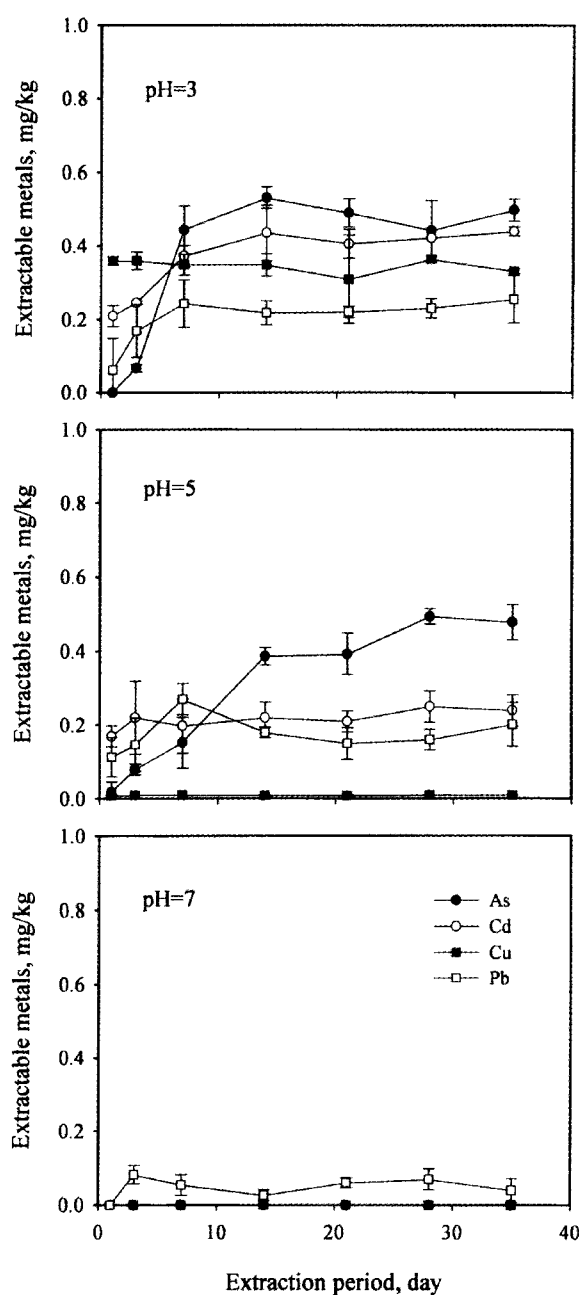


Fig. 1. Water extractable heavy metals in phosphogypsum samples of three different pHs.

sed as the pH of phosphogypsum increased. In the phosphogypsum of pH 7, amounts of water extractable metals were nearly zero except Pb of about 0.05 mg/kg. There was no significant difference in the amount of extractable metals during the extraction period of 5 weeks except the initial short period. The fact that length of extraction time does not affect heavy metal extractability means that there may be small fractions of easily soluble or extractable forms of metals in the phosphogypsum and most of the other frac-

tion would be very insoluble in water.

In addition to the water extraction, DTPA solution extractable metals were also investigated and the results were presented in Fig. 2. The DTPA soil test procedure is among the more widely used techniques to identify soils with inadequate levels of available metals. The DTPA molecules form water-soluble complexes with free metal cations and, thereby, decrease the cation activities in solution¹⁴. In response, cations desorb from soil surfaces or dissolve from labile solid phases to replenish solution cations. Therefore, DTPA extraction would be a more reasonable estimation of metal availabilities in soils amended with phosphogypsum than the water extraction.

The extractability of metals in DTPA solution was not quite different, but a little higher in comparison to the water extraction, especially at pH 7. As found in the water extraction, extractability of heavy metals was highest in the phosphogypsum of pH 3. And as pH increased the extractability decreased. In the phosphogypsum of pH 7, water extractable metals were negligible, but 0.1~0.2 mg/kg of Cu and Pb and 0.05~0.08 mg/kg of Cd were extracted in the DTPA solution. Extractability of As was significantly lowered at pH 7.

There was also no significant difference in the amount of DTPA extractable metals during the extraction period of 5 weeks. Considering the complexation of DTPA molecules with free metal cations, if there were further soluble forms of metals in the extraction mixture after the initial short-term extraction, metal extraction should be further increased with increasing period of extraction. But the length of extraction time did not affect the metal extractability. Therefore, this result further confirm the fact that there may be only a small amount of soluble or extractable forms of metal in the phosphogypsum.

Extractable fractions of the heavy metals in terms of total amount of the metals in phosphogypsum are presented in Table 2. Extractability was highest for As and lowest for Pb. The extractability of each metal was significantly decreased as pH of phosphogypsum increased, and all of the metals in phosphogypsum of pH 7 were almost insoluble in water and less than 6% were soluble in DTPA solution.

Phosphogypsum contains more than 93% of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and $0.94 \sim 1.56 \times 10^{-3}$ M of SO_4 was extracted in the water and DTPA solution. Sulfate compounds of Cd and Cu are freely or very soluble in aqueous solution, and PbSO_4 has the solubility product of 1.6×10^{-8} . The lower solubility of metals could be due to the precipitation of

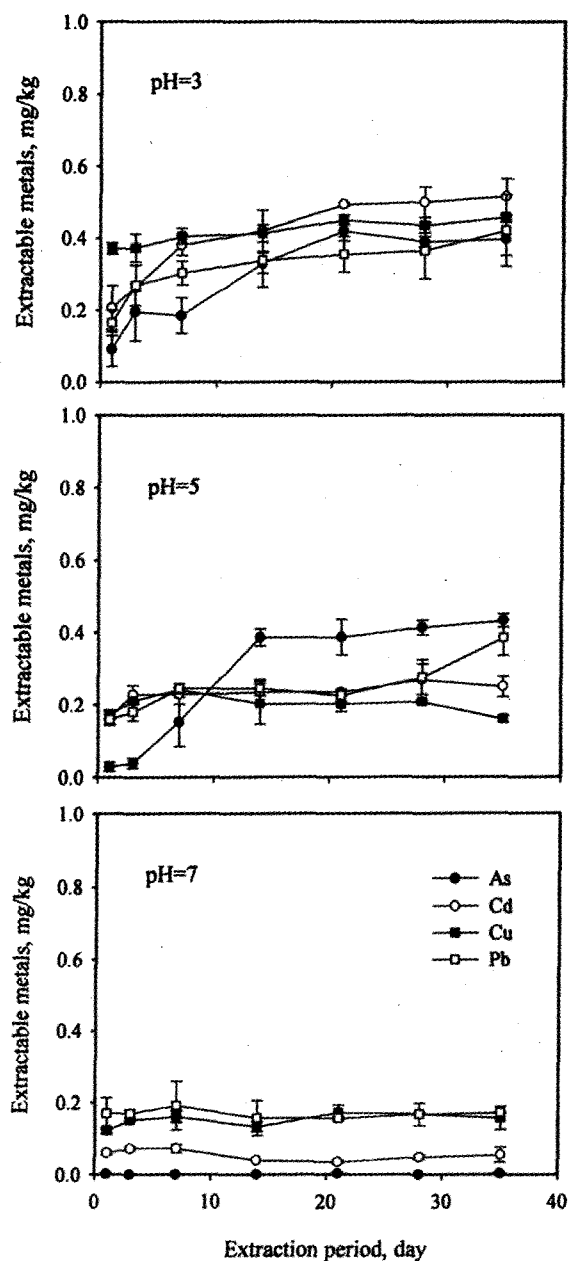


Fig. 2. DTPA solution extractable heavy metals in phosphogypsum samples of three different pHs.

metal sulfates, but the concentrations of Pb in the extracts were in the range of $2 \sim 4 \times 10^{-7}$ M, and considering the solubility product of PbSO_4 , precipitation of PbSO_4 in the extraction solution is impossible. This consideration also conforms the fact that phosphogypsum contains only small fraction of easily soluble or extractable forms of the hazardous metals.

Amounts of available contaminant elements in soil treated with phosphogypsum were measured by Chung et al.⁹. Levels of available contaminant elements in the soil treated

Table 2. Extractability of heavy metals in water and 0.005 M DTPA solution after extraction of 5 weeks. Data are percentages of total amount of each metal in phosphogypsum.

Metals	Water extraction			DTPA extraction		
	pH 3	pH 5	pH 7	pH 3	pH 5	pH 7
	%					
As	71.1	68.4	0.0	56.8	61.7	0.5
Cd	31.4	17.1	0.0	37.1	17.1	3.9
Cu	12.7	0.4	0.0	17.5	6.2	6.0
Pb	5.4	4.3	0.9	8.9	8.2	3.6

with phosphogypsum were quite low, and not different from the levels found in the control soil both in the laboratory and field experiments. Ha et al. also found that application of the mixture of fly ash and phosphogypsum in agricultural land did not increase the levels of available heavy metals in soil⁵). Concentrations of contaminant elements in the leaf of melon grown in soils treated with phosphogypsum were not significantly different comparing to the metal concentrations in the plant grown in control soil. Also the levels of metals in the leaf of melon were relatively lower comparing to the levels in crops grown in soils treated with fly ash or composts of municipal sewage sludge^{12,15}). Although rock phosphate, particularly from Florida, often contains substantial quantities of Cd, this Cd appeared to be of no concern environmentally in terms of the content in grain, being only a fraction of values reported in situations where Cd has been added to soil as municipal sludges or as phosphate fertilizers^{16,17}). Therefore, phosphogypsum should present no environmental problems in terms of contaminant elements when used at appropriate rates for agricultural purposes.

CONCLUSIONS

In addition to supplying the essential elements, Ca and S, phosphogypsum can have profound effects on both the physical and chemical properties of certain soils. Such soils frequently have one or more of the following characteristics: 1) dispersive top soils which readily form crusts, or 2) subsoil hardpans which limit root penetration or 3) acid subsoils in which high levels of soluble aluminum and low levels of Ca prevent root proliferation. However, no widespread use of by-product phosphogypsum will be made unless such uses pose no threat to the public health and soil contaminations.

Although the possibility of hazardous element contami-

nation has hindered agricultural use of phosphogypsum, total contents of heavy metals including As, Cd, Cu and Pb were in the ranges of those metal contents in natural upland soils and heavy metals extractable in water and DTPA solution were also very small in phosphogypsum.

These results suggest that the application of phosphogypsum at appropriate rates on agricultural lands appears of no concern in terms of hazardous element contamination in soil.

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