Agricultural Uses of Phosphogypsum, Gypsum, and Other Industrial Byproducts

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This chapter provides information about several industrial byproducts and agricultural uses for these byproducts. The focus is on relatively new industrial byproducts for which significant data have accumulated over the past 10 to 15 yr. Also included are some byproducts that have received little if any attention in the past, for example, urban-oriented residues from concrete manufacturing and fines from the production of rock aggregate. Most of these byproducts may present little if any hazard in agriculture. Parr et al. (1983) and U.S. Department of Agriculture (1978) provide information on industrial byproducts not covered in this publication. These two sources include information on byproducts from the following industries: petroleum, pharmaceutical, pulp and paper, soap and detergent, munitions and explosives, pesticides and organic chemicals, textiles, wood preservatives, milling, meat packing, and canneries.

Phosphogypsum

Phosphogypsum is a byproduct of the phosphate fertilizer industry and emanates from the production of phosphoric acid from rock phosphate. Production of phosphogypsum in Florida is estimated to be 27.2 million Mg annually (Hunter 1989). The composition of phosphogypsum varies depending upon the source of rock phosphate and the process for manufacturing phosphoric acid (Mays and Mortvedt 1986). The approximate composition of phosphogypsum is shown in table 29.

Phosphogypsum material normally has an aqueous pH between 4.5 and 5.0. One problem with using phosphogypsum in agriculture is that it contains radioactive radium and radon. In the late 1980's, the agricultural use of phosphogypsum was suspended by the U.S. Environmental Protection Agency when the agency reduced the level of allowable radioactive radium-226 and associated radon in phosphogypsum by a factor of five. This restriction put some of the phosphogypsum into the nonallowable category and

Table 29. Composition of phosphogypsum

Major constituents (g kg^{-1})[*]:

Ca	200–240
P	1–5
S	150–190
F	5–38

Minor constituents (mg kg^{-1})[*]:

K	100–800
Mg	8–400
Mo	65
Cd	0.23

Radioactive elements:

^{226}Ra	10–25 pCi g^{-1}[†]

[*] Values are averages of those presented in Mays and Mortvedt (1986), Pavan et al. (1987), Lin et al. (1988), Alva and Sumner (1989), Alva et al. (1990), and Sumner (1990).

[†] Value is from Mays and Mortvedt (1986) and is for southern Florida phosphogypsum only.

therefore made phosphogypsum illegal for agricultural use (U.S. Gypsum Company 1990). Since then the U.S. Environmental Protection Agency (Federal Register 6/3/92) has permitted the controlled use of phosphogypsum in agriculture if radium-226 levels are <10 pCi g^{-1}. This restriction on the maximum radium radioactivity essentially eliminates the use of southern Florida phosphogypsum because its radium-226 levels are commonly in the range of 15 to 25 pCi g^{-1}. The restriction does not impact phosphogypsum from northern Florida or North Carolina, which generally have lower levels of radium-226 (Richardson, personal communication 1992).

The fate of radium-226 in Florida phosphogypsum was investigated by Mays and Mortvedt (1986). They applied phosphogypsum containing 25 pCi g^{-1} ^{226}Ra at rates up to 112 Mg ha^{-1} to the surface of a silt loam soil and grew successive crops of corn (*Zea mays* L.), wheat (*Triticum aestivum* L.), and soybean (*Glycine max* L.). Application of phosphogypsum even at the 112 Mg ha^{-1} rate had no effect on the radioactivity levels in grain of corn, wheat, or soybeans. The 112 Mg ha^{-1} rate was more than 200 times the normal rate of gypsum used for peanut fertilization. Additionally, they noted no increases in grain Cd levels, but at the highest rate they found that corn growth slowed. They speculated that the slower growth was due to an imbalance of Ca and Mg.

Numerous studies have shown that phosphogypsum can alleviate some detrimental effects of subsoil acidity on plant growth (Alva and Sumner 1989, Alva et al. 1990) when surface applied (Caldwell et al. 1990) or subsoiled (McCray et al. 1991). Sumner (1990) concluded that there was essentially no difference between mined gypsum and phosphogypsum regarding correction of subsoil acidity problems.

Lin et al. (1988) used a mesh bag technique to examine the effect of phosphogypsum versus lime on alleviating poor root growth in a Spodosol B_h horizon. Soil in mesh bags was amended with either lime or phosphogypsum, and the bags were implanted around mature orange trees and sampled for periods up to 139 days. The B_h horizon amended with lime had significantly higher root densities than control soils, but root densities in phosphogypsum-amended soil were not significantly different than those of controls. In this study, phosphogypsum did not decrease exchangeable Al compared to control soils.

Pavan et al. (1987) compared the effect of applications of phosphogypsum, lime, calcium chloride, or magnesite (a magnesium-lime material) on apple trees (*Malus domestica* Borkh.) growing in Brazilian soils. Phosphogypsum and lime significantly increased rooting density in the surface of a high-aluminum soil, but this effect extended to a depth of 60 cm with the phosphogypsum application. Phosphogypsum or lime application significantly increased fruit size and yield compared to other treatments, reflecting the enhanced rooting and increased water supply to the trees.

Sumner (1990) compared the effects of surface application of phosphogypsum vs. mechanical mixing of the soil or mechanically mixing lime into a coarse sandy loam soil with an argillic horizon in the subsoil. Peaches exhibited only a slight response to surface phosphogypsum application but responded significantly to both mechanical treatments. The lack of response to gypsum was credited to the greater sensitivity of peach roots to physical rather than chemical barriers in the subsoil.

Gypsum

Gypsum ($CaSO_4 \cdot 2H_2O$) occurs geologically as an evaporite mineral associated with sedimentary deposits. The most important property of gypsum relating to agricultural applications is its solubility. Although gypsum is only slightly soluble in aqueous solution

(solubility of 2.5 g L^{-1} in water), it is more soluble than calcite ($CaCO_3$, solubility of 0.15 mg L^{-1} in water) (Finck 1982). The benefits of gypsum on soil chemical and physical properties are as follows:

Physical benefits	Chemical benefits
Increased infiltration	Increased subsoil Ca
Increased aggregation	Decreased subsoil acidity
Decreased Na adsorption	Reduced exchangeable Al
Reduced root impedance	
Reduced restriction of hardpans	

Reviews on the use of gypsum in agriculture have been published (Oster 1982, Shainberg et al. 1989). However, these reviews mostly discuss the effects on agronomic crops rather than the effects on soil properties. The ameliorative effect of increased surface infiltration from surface-applied gypsum on dispersive and sodic soils is well documented (Kemper and Noonan 1970, Shainberg et al. 1989, Roth and Pavan 1991). Applied gypsum decreases the percentage of Na adsorbed on the soil and increases the free electrolyte concentration; these two effects lead to reduced dispersion and increased flocculation and aggregation of soils (U.S. Department of Agriculture 1954). In high-sodium soils with a pH between 8.5 and 10, applied gypsum raises the soluble Ca concentration to levels greater than that of calcite, thereby precipitating calcite. In turn, pH is reduced to 7.5 to 8.0, and calcite and gypsum coexist. The higher soluble Ca concentrations lead to enhanced flocculation of soil colloids (Lindsay 1979).

The effect of surface-applied gypsum (10^4 kg ha^{-1}) on subsoil mechanical impedance was studied by measuring changes in cone penetrometer index for 2.5 yr after application (Radcliffe et al. 1986). A significant reduction in mechanical impedance and increase in root penetration was noted to a depth of 0.55 m within this relatively short time frame. The marked improvement in root penetration resulting from the gypsum appeared to be more directly related to increased Ca supplied by gypsum, which is known to be essential for rapid meristematic root growth. Greater root growth means that more organic matter is being produced in the soil, and this organic matter aids in aggregation and promotes the invasion of beneficial mesofauna such as earthworms. Earthworm burrows facilitate movements of water, oxygen, and carbon dioxide essential to crop growth.

Gypsum has received considerable attention because of its ability to ameliorate subsoil acidity and therefore improve plant rooting (Sumner and Carter 1988). The primary problem associated with subsoil acidity is the high level of phytotoxicity from soluble Al and, to some extent, from soluble Mn. In some cases these high levels of Al and Mn are related to deficiencies of Ca (McCray and Sumner 1990). Gypsum additions can lead to both negative and positive plant responses (Alva et al. 1990), indicating that the chemistry of gypsum in the soil system is not yet completely understood (McCray and Sumner 1990).

Gypsum provides both Ca and S for crop nutrition and has long been used as a Ca source for peanuts (*Arachis hypogaea* L.). Peanuts have a unique Ca requirement during pod development (Alva et al. 1989), depending on peanut type (Gaines et al. 1991), soil Ca status (Alva et al. 1991), and type and form of applied gypsum (Alva et al. 1989). Repeated annual applications of gypsum to peanuts, however, can cause a P deficiency (Sistani and Morrill 1992), since buildup of excess Ca in soil may cause the P to be "tied up" in the form of calcium phosphate.

Gypsum increased Ca levels in cauliflower (*Brassica oleracea botrytis* L.) but had no effect on reducing tip burn, a physiological disorder commonly associated with Ca deficiency (Rosen et al. 1987). The importance of gypsum being more soluble than calcite was shown by Carter and Cutcliffe (1990) in brussels-sprouts (*Brassica oleracea gemmifera*) grown in a low-calcium soil. Gypsum raised tissue Ca levels and marketable yields significantly during the first growing season after application whereas the effects of calcite took longer.

Gypsum was added to blueberry (*Vaccinium* sp.) to study the effect of adding Ca on upland mineral soils without significantly affecting soil pH (Korcak 1992). Although the blueberry is considered to be acid loving, it showed at least a short-term tolerance for increased soil Ca from gypsum. The practicality of using gypsum to enhance root tolerance to high levels of Al in acid upland soils is under further study.

Continuous applications of gypsum or high rates of surface application can cause problems. One of the problems is excessive Ca buildup, which can induce P deficiency and cause excessive leaching of Mg and K from the surface, particularly in sandy soils. Korcak (1988) applied a high-gypsum byproduct between the

rows in an orchard for 6 yr and found that foliar Mg levels were becoming deficient. Deficiencies of P, Mg, or K will cause various plant symptoms, including reduced yield. Another problem with continuous or high application rates is increased soil salt content, which can also damage plants and stunt their growth. Sometimes the so-called disadvantages of a material, however, can be used to the grower's advantage, depending on the crop and the nutrient level of the soil. For example, Alva and Gascho (1991) added gypsum to peanuts and found that the induced leaching of Mg and K was beneficial to the crop's growth.

The best way to avoid damaging a crop from gypsum applications is to develop standardized soil analyses that will allow for the determination of safe application rates. Sumner (1990) proposed a soil test that is based on the soil's ability to absorb salt. The test is based on the fact that soils showing a favorable response to gypsum are the ones capable of absorbing the most salt. The test, however, still needs to be calibrated and standardized for a wide range of soil types.

Leather Manufacturing Byproducts

Leather manufacturing generates about 150,000 Mg of dry sludges annually (U.S. Environmental Protection Agency 1976). Basically, three types of byproducts are produced: solid wastes from splitting and trimming hides; sludges from liming, dehairing, pickling, and chrome tanning; and liquid wastes from each step in the operation (Hughes 1988).

The primary agricultural constraint on the use of byproducts from leather manufacturing has been the Cr content of the sludges. Currently, most processing plants are recycling the Cr in wastes before they leave the plant. This recycling segregates high-chromium waste streams from the other waste streams. Chromium has been of concern due to its potential plant toxicity. Trivalent Cr (CrIII or chromic) is present in the sludges but is not toxic to plants and is immobile in the soil system. However, hexavalent Cr (CrVI or chromate) is phytotoxic and mobile. The possible oxidation of trivalent Cr to the mobile form and the potential for phytotoxicity has been the primary focus of most of the research for agricultural use of leather manufacturing wastes (Chaney 1983).

Another potential problem is the salinity of the waste-water generated. This salinity originates from salt

present in the hides prior to tanning. Untreated, this wastewater is not suitable for agricultural use. This problem may be circumvented by composting the wastewater and sludge. Under high rainfall regimes, leaching will occur and salinity of the compost will decrease to acceptable levels.

Dewatered tannery sludge has N contents ranging from 2.5 to 5 percent. When Cr has been adequately excluded from these sludges, the optimum application rates for this sludge should be based on N needs of the crops to be grown. This approach should prevent excessive nitrates from being in soil solution during times when they can be leached into groundwater (Stromberg et al. 1984).

Calcium Silicate Slag

Calcium silicate slag is a byproduct of the production of phosphate from apatite ore in an electric furnace. The slag material has a calcium carbonate equivalent of almost 50 percent and contains trace amounts of unrecovered P along with Ca, Mg, and K plus plant micronutrients. However, the Si content of the material has drawn the most research attention.

Sugarcane and rice are known to produce maximum yields when supplemented with Si (Anderson et al. 1992). Calcium silicate slag, containing about 200 g Si kg^{-1}, has been used successfully as a Si source. In addition to yield increases, Raid et al. (1992) reported enhanced resistance of sugarcane to ringspot (a foliar disease) from the use of calcium silicate slag. They hypothesized that the increased uptake of Si into the leaves helped to create a penetration barrier to certain attacking insects that are disease carriers.

The concentration of unrecovered P in calcium silicate slag is usually less than 10 g kg^{-1}. However, if high amounts of slag are applied to agricultural lands, significant amounts of P will be applied. Much concern has arisen over adverse environmental effects from excessive P fertilization in the Florida Everglades, where sugarcane production is high. The fate of P applied from calcium silicate slag has been studied (Anderson et al. 1992). At application rates of up to 20 Mg ha^{-1}, P applied in slag was found to be biologically inactive and not likely to contaminate drainage waters and waterways.

The concern over adverse environmental effects of increased P in waterways is not limited to the Ever-

glades area. The potential of high-calcium industrial byproducts, such as calcium silicate slag, to reduce solubility of P and keep its concentration in biologically desirable ranges needs to be documented. This type of research is also needed for other high-calcium byproducts such as fluidized bed materials and flue gas desulfurization byproducts from coal-burning power plants.

Anderson (1991) found another potential problem with the agricultural use of calcium silicate slag. In some cases following slag application, Mg deficiency can occur and yields can be subsequently reduced. It is unknown whether this is due to a Si/Mg antagonism, a low soil Mg content, or possibly an imbalance of soil Ca and Mg resulting from the high ratio of Ca to Mg in the applied slag.

Incineration Ash

Incineration of municipal wastes is becoming more widespread. As of 1990 there were 70 municipal refuse incinerators operating in the United States and about 250 facilities in the planning stage (Lisk et al. 1989). Ash materials from incineration are becoming an urban problem. No reports exist on the potential for agricultural use of incinerator ash. Most of this ash will probably be placed in landfills.

The incineration processes used vary from facility to facility, thereby creating ashes with a range of characteristics (for example, ranging from acidic to alkaline). The variability of the end product is one of the primary reasons for not using this ash for agricultural purposes, particularly because of variability in the content of trace elements (Swahney and Frink 1991). Pressures to apply these ashes to land will increase in the future, and therefore baseline data to identify the benefits and hazards of these materials will be needed.

Concrete Manufacturing Residues

Approximately 1.8 Mg of concrete are produced each year per person in the United States, and about 2 to 4 percent of this amount, 36.3 to 72.6 kg per person, is waste. Concrete waste is generally an urban byproduct. For example, in the Washington-Baltimore corridor it is estimated that about 9,000 Mg of concrete waste is produced annually. A portion of concrete waste originates from the solid materials (aggregates used in the concrete) rinsed from delivery trucks. This material is alkaline and high in calcium silicates.

A preliminary investigation of the solid material from truck rinsing is underway (Korcak, unpublished data). Initial results indicate that the material is not phyto-toxic even at rates up to 224 Mg ha^{-1} when applied to the surface. As a result of its alkaline and calcareous nature, this material appears to have potential as a liming agent.

Aggregate Industry Fines

The annual production of aggregate materials (sand, gravel, and crushed stone) in the United States is about 1.8 billion Mg (R. Meininger, personal communication 1993), and about 5 to 10 percent of this total is waste fines. The size of these fines ranges from that of fine sand to that of clay, and the fines are collected in settling ponds. Many types of aggregate materials are produced in the United States, partly because of the large number of production plants (Tepordei 1987) and the number of different rock types that are crushed (Tepordei 1992).

A number of attempts have been and are being made to find uses for aggregate materials. Some of the fines are mixed with an organic material (for example, mixed with municipal biosolids or composted with municipal refuse) to create a manufactured top soil.

When rocks fracture, nutrients within the rock material become more available. Enhanced availability is evidenced by the proliferation of root growth in new fractures in rocks. Plant growth and nutrient availability can be increased by incorporating fines from rock crushing operations into soils. Exudates from roots may have a role in mobilizing nutrients from newly fractured mineral surfaces. Information is needed on how much of this mobilization is caused by water and how much is caused by root exudates. This information will assist in understanding and predicting the benefits and possible hazards of agricultural use of freshly crushed fine materials or fines at depths that have not been demineralized by plant growth or acid leaching.

Wood Ash

The combustion of wood waste for producing steam or electricity creates localized sources of ash. An industry rule-of-thumb is that bark from 1 million board feet of logs will provide 1 ton of ash. This equates to more than 908 Mg of ash generated annually in western

Montana (Host and Pfenninger 1978). Nationally, 1.4 to 2.7 million Mg of ash are produced yearly from combusting wood wastes from paper mills and saw mills (Campbell 1990).

Ash composition varies with the source of waste wood. Etiegni and Campbell (1991) reported that lodgepole pine sawdust ash had a pH of about 13 and contained 18 to 26 percent Ca, 6 to 9 percent Mg, 0.4 to 11 percent K, and 1.7 to 2.5 percent P. They studied the effect of temperature on ash composition and found that Ca, Mg, and P in ash increased with increasing temperature while K decreased. Schreiner et al. (1938) noted that some unleached hardwood ashes can contain upwards of 6 percent potash, 2 percent phosphoric acid, and 30 percent lime.

Agricultural use of wood waste has increased and will continue to increase due to stricter regulations on open burning or landfilling and due to increased costs of disposing of these materials in landfills. A number of studies performed on the use of wood ash in agricultural situations have been summarized (Campbell 1990). The primary benefits of wood ash include neutralizing soil acidity (lime potential) and providing a source of K plus other macronutrients and micronutrients. Rates for applying ash to land should be based on the soil lime requirement. Applied at the proper rate, ash should present little risk to the environment.

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