

ANALYSIS OF SYNTHETIC GYPSUM

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Preface

Gypsum is one of the earliest forms of fertilizer used in the United States. It has been applied to agricultural soils for more than 250 years. Gypsum is a moderately soluble source of the essential plant nutrients, calcium and sulfur, and can improve overall plant growth. Gypsum amendments can also improve the physical and chemical properties of soils, thus reducing erosion losses of soils and nutrient concentrations (especially phosphorus) in surface water runoff. Gypsum is the most commonly used amendment for sodic soil reclamation and can be included as a component in synthetic soils used in nursery, greenhouse, and landscape applications. These multiple uses of gypsum represent potential benefits to agricultural and horticultural users.

Currently, a large amount of flue gas desulfurization (FGD) gypsum is produced by removal of sulfur dioxide (SO_2) from flue gas streams when energy sources, generally coal, containing high concentrations of sulfur (S) are burned. Initially, most of the FGD gypsum produced in the United States was used in the wallboard industry and only a small amount was used in agriculture. However, FGD gypsum is suitable for agricultural uses and, similar to mined gypsum, can enhance crop production. As with other fertilizers and agricultural amendments, FGD gypsum must be used appropriately to avoid potential negative impacts on both agricultural production and the environment. In many respects, there are similarities between the agricultural use of FGD gypsum and nitrogen fertilizers in that both can provide crop production benefits but, if improperly used, can also lead to negative environmental impacts.

Abstract

The use of industrial byproducts as construction material can help to achieve sustainability in this industry. Phosphogypsum (PG) is a waste obtained in the phosphoric acid (PA) manufacturing process, produced in large quantities, especially from the soil fertilizer industry. Alternatively, in the disposal of these materials in landfill, several investigations have applied PG as a substitute for natural gypsum in the production of Portland cement to control the hydration reaction rate of cement and also in concrete, bricks, plaster panels, and others. The composition and characteristics of PG are closely related to both the composition and origin of the feedstock used (phosphate rock), showing high gypsum content, and high levels of natural radionuclides, especially from U-series. These properties depend on the PA production process and

the origin of the raw material. In this chapter, the possibilities of using this waste in cement-based materials are presented, to encourage future research lines based on this waste/byproducts

Types of artificial gypsums

Artificial gypsum (AG), also named synthetic gypsum, is a co-product obtained from different industrial processes, and it is mainly composed of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). AG generally shows similar characteristics to natural gypsum (NG) and, in many cases, can be substituted by these AGs. Large amounts of AG are produced around the world in many industrial processes. The main current industrial process generators of AG are shown in Table

Industrial processing Gypsum generated

Phosphoric acid	Phosphogypsum
Titanium dioxide	Titanogypsum
Boric acid	Borogypsum
Fluoride acid	Fluorogypsum
Citric acid	Citrogypsum
Soda by using Solvay method	Soda gypsum
NaCl from seawater	Salt gypsum
Phenol	Phenologypsum
Flue gas desulfurization	FGD gypsum

AG can contain high levels of impurities and pollutants, such as phosphates, fluorides, alkalis, boron, naturally occurring radionuclides, heavy metals, and trace of other elements. They are often stored in landfills. These places could be used in the future as AG mines and for developing valorization and recovery applications to be used for new material manufacturing. Therefore it is important to take current regulation into account, the main waste regulation in Europe being the EU Directive 2008/98/EC of November 19, 2008, on Waste, which in Article 1 (Subject matter and scope) says: “This Directive lays down measures to protect the environment and human health by preventing or reducing the adverse impacts of the generation and management of waste and by reducing overall impacts of resource use and improving the efficiency of such use.”

This Directive also defines the concept of recovery (or valorization) as: “any operation the principal result of which is waste serving a useful purpose by replacing other materials ...” In addition, Article 6 of Directive 2008/98/EC establishes the concept of the “end-of-waste,” according to the following: “Certain specified waste shall cease to be waste when it has undergone recovery, including recycling, operation and complies with specific criteria to be developed in accordance with some conditions.”

In addition, one of the strategic lines of the European Union policies aims at ensuring the “Circular Economy” through the efficient use of raw material, residues, and the generation of clean energies. For that reason, policies on waste management must be aimed to respect the hierarchy established by the regulation: reduction, reuse, and recycle. In addition, environmental benefits provided by adequate waste recovery represent an excellent alternative to its management.

The use of AG in the manufacturing of new materials and products will create many positive economic and environmental benefits. Economically, this will generate revenue from a product that otherwise incurred waste management costs. And by creating a valuable product from waste, material is kept out of landfills, and environmental pollution is reduced. Furthermore, increased use of AG as a substitute for NG will conserve and reduce the need to mine natural resources. AG products even have benefits over NG products in terms of costs and environmental impacts.

Keeping in mind everything mentioned earlier, the valorization of AG as secondary raw materials for the manufacture of new environmentally and friendly systems will contribute to the fulfillment of overall environmental objectives, and especially to the sustainable development of the activities related to the environment. Thus it will be essential to develop new materials and production technologies that imply a sustainable and eco-efficient alternative for gypsum waste.

Sources of synthetic gypsum

Synthetic gypsum, which is now used in about 30% of drywall, is a by-product of coal-fired power plants. It is sometimes confused with fly ash another coal combustion product with which it has very little in common.

Properties of Gypsum That Provide Benefits for Agricultural Uses

To make recommendations for gypsum use in agriculture, it is important that we have a good understanding of its composition and properties. Composition of pure gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is 79% calcium sulfate (CaSO_4) and 21% water (H_2O). Pure gypsum contains 23.3% calcium (Ca) and 18.6% sulfur (S). Gypsum is moderately soluble in water (2.5 g per L) or approximately 200 times greater than lime (CaCO_3). This makes the calcium in gypsum more mobile than the calcium in lime and allows it to more easily move through the soil profile.

FGD Gypsum as a Source of Plant Nutrients For many years, crops received more than enough sulfur from rainfall, but monitoring of sulfur deposited by rainfall onto soil has revealed significant decreases in sulfur inputs. In 1979 about 31 lbs of sulfur per acre were deposited onto our soil in Ohio, and this decreased to

about 16 lbs of sulfur per acre in 2007 (Figure 2-1). This decrease—coupled with other decreases in S inputs due to the use of highly concentrated fertilizers containing little or no sulfur, intensive cropping systems, and increased crop yields that result in more sulfur removal from the soil every year—is leading to more and more reports of sulfur deficiencies in crops.

FGD Gypsum to Improve Soil Physical Properties

Soil structure is defined as the arrangement of primary mineral particles and organic substances into larger units known as aggregates with their inter-aggregate pore system. Soil structure has been shown to influence a wide variety of soil processes including water and chemical transport, soil aeration and thermal regime, erosion by wind and water, soil response to mechanical stress, seedling germination, and root penetration.

Many soils from semiarid to humid regions have an unstable structure, which makes them susceptible to erosion and difficult to manage. These soils have a tendency to disperse and form a stable suspension of particles in water. As a result, they develop a more compacted structure, particularly at or near the soil surface. Clay dispersion is caused by the mutual repulsion between the clay particles ‘which results from the presence of extensive negative electric fields surrounding them (Dontsova et al., 2004). Flocculation is the opposite process, where the electric double layer is sufficiently compressed so that attractive forces allow coagulation of the individual clay particles into microaggregates. Application of gypsum can reduce dispersion and promote flocculation of soils. Flocculation is a necessary condition for the formation and stabilization of soil structure. This increases water infiltration and percolation, thus reducing soil erosion and improving water quality.

Gypsum to Improve Soil Chemical Properties

The detrimental effects on plant growth of subsoil acidity, particularly at high levels of exchangeable aluminum (Al^{3+}), are well known. The lower the soil pH, the greater the concentration of soluble and available aluminum.

For many plants growing in acid soils, it is not the pH that is especially toxic, but the presence of high levels of exchangeable aluminum (Figure 2-7). Subsoil acidity prevents root exploitation of nutrients and water in the subsoil horizons. Agricultural lime is recommended for correction of soil acidity and low soil pH. Whereas the beneficial effects of calcitic lime are mostly limited to the zone of incorporation, surface applications of gypsum may affect soil physical and chemical properties at depth. This is because of gypsum’s much greater solubility compared to lime

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