

Summary

The papers in this publication may be divided into two parts; one dealing with procedures to determine the chemical composition and the physical properties of gypsum and gypsum products, and the other dealing with issues associated with the utilization of by-product gypsums.

Kocman has developed a rapid and precise X-ray fluorescence method for the multi-element analysis of gypsum and its products. Specimens of gypsum are calcined and fused into flat transparent disks, with sodium tetraborate flux. This flux was chosen because it produces and reduces clear transparent disks without the high incidence of gas entrainment and cracking. However, the use of sodium tetraborate prohibits sodium analysis by this method. Elements susceptible to analysis are calcium, sulfur, magnesium, strontium, silicon, aluminum, iron, potassium, phosphorus, and chlorine. The instrument used in the study was a Philips PW-1400 wavelength dispersive spectrometer equipped with four crystals (LiF, Ge, PET, TIAP). The analytical method is suitable for gypsum rock, hemihydrate, anhydrite, wallboard cores, gypsum bricks, gypsum plasters, quickset fillers, specialty gypsums, gypsum-based flooring cements, and other gypsum products.

Green describes a rapid and accurate polarizing microscope procedure for the qualitative analysis of gypsum, its dehydration products, and some common impurities. Gypsum may be identified by the refractive indices, oblique extinction angle, birefringence index, and a blue dispersion staining color. Natural anhydrite generally appears as blocky crystals with distinctive refractive indices, birefringence index, and parallel extinction. Beta hemihydrate has the same shape as the original dihydrate but is porous and cloudy instead of clear and solid. Alpha hemihydrate has characteristic refractive indices, a specific birefringence index, and its color changes from orange to blue when rotated. Deadburned gypsum has a similar refractive index to natural anhydrite but may be identified by dispersion colors of red and blue. Soluble anhydrite is the one species difficult to identify on the polarizing microscope. Silica has the same birefringence as gypsum, but its refractive index is higher and it has a yellow dispersion color. Limestone may be identified by its very high birefringence index whereby calcite may be distinguished from dolomite by color.

Goswami and Chandra identify sources of error in the determination of sulfur trioxide in gypsum by the precipitation of barium sulfate, and recommend a

revision of Section 12 of ASTM Chemical Analysis of Gypsum and Gypsum Products (C 471). The authors argue that the ASTM method, in using 50 mL of 1 + 5 hydrochloric acid as solvent for a 0.5-g specimen of gypsum and 20 mL of 10% barium chloride solution to precipitate, provides too high a concentration of both acid and chloride ions. The method also does not specify the final volume of solution before precipitation nor the use and type of filtering crucible. Lowering the quantities of hydrochloric acid and barium chloride used would reduce occlusion of chloride ions, coprecipitation of barium chloride and Ca^{++} , and solubility of barium sulfate in acidic solution. The authors recommend the following:

1. Reduce the initial amount of hydrochloric acid used as solvent to 25 mL of 1 + 5 hydrochloric acid for the 0.5-g test specimen.
2. Use 20 mL of 6% barium chloride solution (preferably old).
3. Make the volume of the reaction solution up to 400 to 500 mL before precipitation of barium sulfate.
4. Use filtering crucibles.

Karmazsin's paper describes a simple apparatus for measuring the degree of hydration of plaster and gypsum rock. The reactor consists of a vertical stainless steel cylinder capable of holding six small stainless steel sample tubes that are suspended from the removable roof of the cylinder by a stainless steel thermocouple well. The cylinder is fitted with a heater controlled by an external thermocouple, and a reservoir containing water vapor at 81% relative humidity is connected to the reactor. The reactor may be used to determine accurately the amount of dihydrate in either gypsum rock or incompletely hydrated plaster.

The work of Turk and Bounini on the mechanism of free-water uptake was intended to improve accuracy in the phase analysis of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ systems. The study determined that the amount of free moisture present is dependent on the physical structure of the sample as indicated by the adsorption and thermodynamic equilibria.

Drying conditions must leave these equilibria unaffected, that is, they must be in a region of the phase diagram where all calcium sulfate phases present remain stable. In microwave drying, this is accomplished by the selective absorption of microwave radiation energy to evaporate water. The study showed that microwave drying gives higher free moisture results than oven drying, indicating that more of the free moisture is removed from the pores of atmospheric calcined gypsum.

As Luckevich and Kuntze point out in their paper, the water demand of stucco is reduced by aging, which reduces the ability of the stucco to disintegrate. The objective of the work was to determine the relationship between water demand and particle size distribution resulting from changes in disintegration during aging. Tests used in determining these relationships were particle size analysis and various types of consistency measurements. The experimental data indicate,

with all other factors constant, that there is an almost linear relationship between water demand and particle size distribution and that the particle size distribution is governed by disintegration.

When aridizing agents or surfactants are used, consistency ceases to be a direct function of disintegration alone, but appears to depend on surface properties and particle morphology. This suggests it may be possible to produce a stucco with low water demand without sacrificing the disintegration necessary to maintain the desired setting and strength properties.

The work of Koslowski and Ludwig on the retardation mechanism of citric acid shows that this retarder has a considerable effect on the microstructure of hardened gypsum. Thus increased additions of citric acid cause a linear increase in the average grain size and a broader grain size distribution. Also, there is a hyperbolic change of the grain shape from long-prismatic to compact, an increased uniformity of grain shape, and a change from sphaerolitic crystal growth to isolated crystals.

The rate of hydration also causes changes in the microstructure. A slow rate causes a more distinct change toward a compact crystal shape. Citric acid addition causes a decrease in the total porosity and an increase in the average pore diameter. As a result gypsum strength was found to decrease with increasing additions of citric acid.

Archer's work on flexural strength, nail pull resistance, and core hardness of gypsum board has demonstrated that maximum load causing failure can be determined with greater accuracy using a constant strain rate rather than a constant stress rate. The correlation of results from either procedure shows that core hardness and nail pull resistance tests provide very similar information on core properties. It is argued that the more sophisticated constant strain rate machines should replace the equipment presently conforming to ASTM Physical Testing of Gypsum Board Products, Gypsum Lath, Gypsum Partition Tile or Block, and Precast Reinforced Gypsum Slabs (C 473).

Wirsching's paper describes a successful industrial process for drying and agglomerating flue gas gypsum. The process is intended to overcome the problems of processing flue gas gypsum, which is available as a moist, finely divided powder exhibiting thixotropic properties when attempts are made to use it. The purpose of the drying stage is to remove the 10% adsorbed surface water, without driving off any of the water of crystallization, with the lowest possible energy consumption in the shortest possible time. The equipment for this process is available.

There is a choice of three methods for successfully agglomerating the finely divided gypsum: pelletizing, extruding, and compacting. Technically and economically the compacting press was found to be the best for the agglomeration of flue gas gypsum. The agglomerated synthetic product was found to be similar to crushed natural gypsum rock. The scanning electron microscope (SEM) was unable to detect the presence of the original crystal structure in the compacted material, so that the initial problems of unfavorable particle size and shape were

overcome. As a result, the flue gas gypsum could be used in the same way as natural gypsum, and the thixotropic properties were completely eliminated.

Pressler discussed the history of by-product gypsum (BPG) utilization from 1972 to 1981. Over these nine years, there was no great change in the annual consumption or end use of BPG, consumption ranging from 610 000 to 750 000 ton/year. Five of the six companies that sold BPG in 1981 produced phosphoric acid from phosphate rock and sulfuric acid, while the sixth plant manufactured titanium dioxide pigment from ilmenite. All six companies are located in agricultural areas of the southern United States where the beneficial use of gypsum in agriculture is well understood.

The major applications in this area are stimulation of legume crops, especially peanuts, improvement in fertilizer utilization, softening of clayey soil, and neutralization of alkaline and saline soils. The 630 000 tons of BPG sold in 1981 is a small proportion of the total 10.4 million tons of crude gypsum produced in the United States in that year. There are indications, however, that BPG use in the United States may be on the increase.

The paper of May and Sweeney reports on work conducted by the Bureau at its Tuscaloosa Research Center on the environmental impacts of phosphogypsum produced by the Florida phosphate industry. Some 304 million metric tons of phosphogypsum by-product from the manufacture of phosphoric acid have been stockpiled to date, and the industry continues to generate 30 million metric tons a year. Samples from approximately 300 m of drill core obtained from mine stockpiles were characterized by chemical analysis, X-ray diffraction, emission spectrography, radiology, and physical testing. The data obtained indicated that phosphogypsum is not a corrosive or toxic hazardous waste according to the definition of the Environmental Protection Agency (EPA).

Thirty-nine elements were detected in the phosphogypsum samples, but concentrations of the elements did not vary with depth within the stockpiles. Radium content averaged 21 pCi/g and varied inversely with particle size.

A second paper by May and Sweeney reports on the second phase of the phosphogypsum study, that is, evaluation of the leaching characteristics of radium and toxic components identified in the phosphogypsum stockpiles during Phase I of the study. This was done by comparing estimated background concentrations of trace elements with concentrations found in the subsurface samples. The study concluded that toxic elements and radium were not being leached from phosphogypsum stockpiles.

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