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INDUSTRIAL HYGIENE SURVEY OF THE PHOSPHATE INDUSTRY IN POLK COUNTY, FLORIDA

Prepared by
Occupational Health Program
and
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Introduction

An in-plant preliminary survey was begun on May 28, 1957, of the phosphate industry located in Polk County, Florida, to obtain available information relating to the magnitude and extent of the health problems associated with the working environment of the industry. The survey resulted from a request from the President of the International Chemical Workers' Union to the Surgeon General of the Public Health Service. To implement the survey a series of meetings was held between representatives of the Florida phosphate industry, the Florida State Board of Health, and the Public Health Service. The survey was conducted jointly by the Occupational Health Program of the Public Health Service, and the Industrial Hygiene Division of the Florida State Board of Health.

Available data was obtained from each plant on:

1. General plant layout, operations and processes.
2. Past and current environmental studies.
3. Environmental programs for the control of occupational health hazards.
4. Number of employees and length of time in industry.
5. Plant employee turnover.
6. Plant job classification.
7. History and physical examinations of employees through company facilities and practicing physicians in the community.
8. Compensable and noncompensable lost time illnesses.

The preliminary survey also afforded an opportunity to confer with several local union officials. All local union officials were contacted during the environmental sampling program in November 1957.

Florida Phosphate Industry

Florida phosphate rock deposits were discovered in 1887 and are located in an area about 50 miles long and 40 miles wide in the central portion of the State. The phosphate deposits consist of pebble, sand and clay and are covered by an overburden of sand and clay varying in depth from 5 to 40 feet. Mining of the rock began in 1890 and today the annual production in Florida is 9 to 10 million long tons per year. In 1952,* over 96 percent of the phosphate rock used in the United States for normal superphosphate manufacture came from Florida. Eighty-two percent of the phosphate rock for triple superphosphate manufacture and 83 percent for wet-process phosphoric acid manufacture also came from this area. The principal mines in Florida are located in Hillsborough, Polk and Hardee Counties but the bulk of the phosphate industry is located in Polk County.

In mining phosphate rock, the overburden is removed by draglines. The phosphate matrix is hydraulically pumped as a slurry to a beneficiation plant where it is washed, concentrated, and screened for size. The wet concentrated ore is transported, usually by rail, to mills where it is dried, and most of it is ground and screened. Most of the dried phosphate rock is shipped by rail, trucks, and ships to plants in other States and foreign countries for chemical uses.

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* Chemical Engineering, 59:142, 1952

The phosphorus content of dried pebble phosphate varies somewhat within different areas of the deposit. Phosphorus, expressed as P_2O_5, varies from about 32 percent to 35 percent. The rock contains over 3 percent fluoride, probably in the form of apatite, less than 5 percent quartz (free silica), and several other minor constituents, such as uranium.

In the production of superphosphate, ground phosphate rock is mixed with sulfuric acid in a batch process to produce a slurry which quickly sets up to form a cake. This is cut out of the "den" and conveyed to the storage area for aging and subsequent shipment. Superphosphate contains about 18 percent to 20 percent available P_2O_5.

Triple superphosphate, containing 45 percent to 50 percent available P_2O_5, is made by acidulating ground phosphate rock with phosphoric acid. This acid is usually made in the same plant by adding sulfuric acid to ground phosphate rock, which produces a slurry of dilute phosphoric acid, containing some sulfuric acid, and calcium sulfate. This slurry is filtered and the filtrate is concentrated in evaporators to yield the desired strength of phosphoric acid. The calcium sulfate slurry usually flows by gravity to settling ponds.

Fluorides, mainly as hydrogen fluoride, are liberated by both acidulation processes. Several companies recover fluorides in one form or another for sale to other users.

Elemental phosphorus was produced at one plant during this survey. The process consists essentially of mixing phosphate pebbles (not ground) with silica stone and coke. The mixture is transported to an electric furnace where the phosphate is reduced to elemental phosphorus vapor. The vapor is condensed, collected under water, and stored for future shipment as liquid phosphorus. The electric furnaces are tapped periodically to remove slag.

Two plants, using different processes, produce a defluorinated calcium phosphate material for animal feed supplements. One plant recovers uranium from phosphoric acid.

Preliminary Survey

Dr. John M. McDonald, Director, Industrial Hygiene Division, Florida State Board of Health; Dr. Lewis J. Cralley, Assistant Chief, Dr. Philip E. Morgan, Medical Services, and Mr. Andrew D. Hosey, Chief Engineering Services, Occupational Health Field Headquarters, Public Health Service, conducted a preliminary in-plant survey of the phosphate plants during the period May 28 through June 7, 1957.

In Polk County, Florida, seven companies mine phosphate rock. All these companies and one other operate dry mills. Seven chemical plants manufacture triple superphosphate, two superphosphate, one elemental phosphorus, and two defluorinated phosphates. Nine companies operate 11 plants in the area and employ about 4,000 persons, exclusive of office and supervisory personnel. Operations observed included: mining, rock processing (washing and flotation), drying, grinding, storage and shipment of phosphate rock; manufacture of sulfuric acid, superphosphate and triple superphosphate, mixed fertilizers, dicalcium phosphate, defluorinated phosphate, potassium silicofluoride, and the storage and shipment of these materials; and the manufacture of elemental phosphorus.

During the past five years, a number of environmental health studies had been conducted in the plants surveyed. Some were conducted by consultatory organizations and others by the plant's own staff. Most of the studies were too limited in scope and had been done too long ago to be of much value to the present survey. At the time of the survey, only a very limited amount of air sampling was being done to evaluate in-plant exposure levels. However, between the time of our visit in May to do the preliminary survey and our return in October to do environmental sampling, a great many of the plants had initiated stack sampling programs and some had extended them to include in-plant air sampling.

Although the majority of companies had instituted some type of program for the control of occupational health hazards, they were seldom continuous or given adequate support. The type of program and its effectiveness varied greatly from plant to plant. Several of the plants had extensive construction programs under way to reduce stack emissions through recovery systems as well as general process improvements. When completed these will lower in-plant concentration levels at several locations.

Employment in the phosphate industry in Florida appeared to be stable compared with other Florida industries. Many of the dry mill and mining employees are "old timers" having remained on the same job for periods of from 15 to 25 years. Most of the chemical plants are quite new, having been built between 1947 and 1957. Most have been in operation 5 to 6 years. It is said that the labor turnover in this industry is very low, with the exception of seasonal employees who work principally in the shipping departments.

It was hoped that many of the companies might have fairly comprehensive medical records which could be collected and statistically analyzed to determine the current health status of the workers. This, however, was not possible because such records did not exist for 91 percent of the workers in that portion of the industry we contacted.

Although 100 percent of the workers had been given pre-employment physical examinations, only 30 percent were offered an opportunity for periodic examinations of any sort. Nine percent were required to participate in a medical program designed to detect asymptomatic early changes which might result from exposure to toxic materials at work. Somewhat less than 1 percent were required to have a periodic physical examination designed to detect injuries or illness which might have resulted from excessive demands on muscles, bones and joints by operation of heavy equipment. For approximately 20 percent of the workers, annual periodic examinations were available on a voluntary basis. Those were done in the doctor's office, in town, on the workers' own time. These examinations were general in nature and not specifically designed to detect job-connected illness. It was estimated that half the workers offered such an opportunity took advantage of it. Persons working with elemental phosphorus were required to have periodic dental examinations twice a year.

Interviews with several local practitioners of medicine did not disclose any systematic out-of-plant study of phosphate worker's health. Although there was one suggestion that there existed an increased incidence of naso-pharyngitis among all inhabitants of one community, phosphate worker and nonphosphate worker alike, no tabulation of cases was offered to prove this point, nor was there general agreement that such was the case.

Much useful information was obtained during the preliminary survey through visual observations and conversations with local labor union officials, workers, plant personnel, and physicians in the area. Based on (1) this information and past experiences of the survey team, (2) conferences with medical and industrial hygiene personnel at TVA's Wilson Dam phosphate plant, and (3) a survey of the literature, it was decided that the most significant health hazards might arise from exposures to dusts, fluorides--both gaseous and particulate, and acid mists. Naturally, the manufacture of elemental phosphorus and certain other phosphate products create exposures to other toxic materials in addition to those listed above.

It was generally agreed among members of the survey team that mining and ore concentration plants need not be included in the air sampling program because both of these operations are wet processes and do not entail exposures to toxic materials. This does not deny the necessity for industrial hygiene surveillance of these operations since it is known that workers mixing flotation solutions, particularly those containing amines, may experience contact dermatitis or develop allergies to these substances.

The sulfuric acid plants were not included in the sampling program for several reasons. Foremost among these is that exposures to excessive concentrations of sulfur dioxide or sulfuric acid mists occurred only when there were leaks in equipment, breakdowns, or during improper operation of the plant. In these instances protection of the workers can be achieved by the use of personal protective equipment, such as gas masks and clothing. The survey team did not detect, either by the sense of smell or skin irritation, any hazardous concentrations of acid or sulfur dioxide.

Uranium recovery operations were not included in this sampling program for two reasons: (1) The Atomic Energy Commission had surveyed these operations for possible radiation hazards, and (2) these operations were essentially wet which reduces the possibility of an inhalation hazard.

Effects of Fluorides on Health

Much is known of the effects of: (1) acute exposures to high concentrations of highly soluble and highly reactive gaseous hydrogen fluoride and silicon tetrafluoride, (2) acute exposures of humans to large amounts of sodium fluoride (accidentally or suicidally ingested), (3) chronic exposures to 1 to 8 ppm fluorine in drinking waters, and (4) exposures of grazing animals to fluorine containing compounds in amounts many times the levels likely to be encountered by humans in their industrial environments. On the other hand, almost nothing has been published regarding health effects in humans from chronic inhalation exposures to relatively low concentrations of gaseous hydrogen fluoride or to varying concentrations of rock phosphate dust.

Threshold Limit Values for these latter substances have been recommended by the American Conference of Governmental Industrial Hygienists but these are not exact or final figures which draw fine lines between hazardous and nonhazardous concentrations. They are intended to be used as guides in the control of health hazards. They only represent conditions under which it is felt that workers may be repeatedly exposed, day after day, without adverse effect on their health. The figure of 2.5 milligrams for fluoride dust or hydrogen fluoride per cubic meter of air refers to a weighted average concentration for an 8 hour working shift and does not represent a maximum which is not to be exceeded even momentarily.

Another type of threshold value which has been suggested is that of the amount of fluoride excreted in the urine, a figure of 4 milligrams fluoride per liter of urine being considered the upper limit of normal fluoride excretion. Low levels of fluoride intake are associated with rapid excretion of almost all fluoride taken into the body but higher levels of intake result in progressively larger body burdens, especially in bony tissue.

The values shown in the tables (Appendix A) do not represent weighted exposures over the full work shift. They are grab samples which may be higher or lower than the weighted average for the job.

Generally speaking, fluorides are regarded as general protoplasmic poisons, but their effect is altered according to the chemical compounds and amounts involved in the specific exposure. Gaseous fluorides, such as hydrogen fluoride and silicon tetrafluoride, are very toxic because of their great solubility and reactivity. Hydrogen fluoride has been shown to be a harmful agent as a pulmonary irritant and as a volatile poison. The undissociated hydrogen fluoride molecule is capable of penetration of the intact skin. The vapor causes tissue corrosion similar to that expected from other highly irritant substances such as hydrochloric acid or sulfur dioxide gas. Solutions of hydrogen fluoride and hydrofluosilicic acid are similarly very corrosive.

One experimental study with animals showed that inhalation exposures to 15 mgs/m^3 hydrogen fluoride for 2½ months caused liver, lung and kidney damage which persisted many months after exposures had ceased. (Machle and Kitzmiller, JIHT 17:223, 1935.)

Human, as well as animal studies, have shown that inhaled hydrogen fluoride and particulate fluorides result in increased levels of fluoride in the body and in increased urinary excretion of fluorides. This does not prove that the body is being harmed but it does mean that the fluoride has traversed the pulmonary membrane to enter the blood stream and by way of the general circulation has been transported to the kidney and excreted.

Although dusts of the almost insoluble fluorides frequently can be inhaled in large quantities without causing much irritation, one of their number, cryolite (Na_3AlF_6) has been shown to be a cause of chronic fluoride poisoning or fluorosis. The concentrations being inhaled in one study approximated 30 - 40 milligrams of dust per cubic meter of air. The outstanding symptoms of fluorosis are loss of appetite, vomiting, constipation, rheumatic pains, and shortness of breath and difficulty of breathing on exertion. In fluorosis the bones also appear more dense in x-ray examination and there may be noted calcification of the tendinous muscle attachments and ligaments. Under conditions of most severe exposure, irregular extra bone on the surface of the bone and bony spurs may be formed.

Since cryolite contains approximately 50 percent combined fluoride in contrast to phosphate rock's 0.4 to 4.2 percent combined fluoride it is not anticipated that these two compounds would have the same order of toxicity. The extent to which milder forms of fluorosis might result from exposure to the lower concentrations of fluorides encountered in rock phosphate is not known.

Environmental Sampling Program

The primary reason for collecting environmental air samples was to obtain data to determine the range and magnitude of concentrations of dusts, gases and other potentially hazardous air-borne substances to which the workers were exposed. The results of air sample analyses, appearing in Appendix A, represent concentrations found only during the specific periods of sampling and are not intended to represent a worker's daily exposure to a single air contaminant or multiple exposures. Furthermore, the results are not an evaluation of the severity of the hazard at any sampling sites. In some cases many of the workers were not actually exposed to the peak concentrations reported since they used personal respiratory protective devices in these areas.

Survey Team

Environmental air sampling was begun on October 14, 1957, by a team consisting of Messrs. Andrew D. Hosey, Herbert H. Jones and Howard E. Ayer, Occupational Health Field Headquarters and Messrs. Robert L. Hebblethwaite and Roe B. Hull, Industrial Hygiene Division, Florida State Board of Health. Two survey teams were formed to expedite the collection of air samples. Each team consisted of one person from the Public Health Service and one from Florida's Industrial Hygiene Division, with Mr. Hosey acting as contact with the plants to arrange schedules and also to assist in the collection of samples with either team, depending upon the size of the plant.

Sampling locations, methods of sampling, and methods of analyses are discussed in Appendix B under these headings. An average of three air samples was collected at each of the sampling locations at each plant on different days.

Results

The results of the environmental air sampling are presented in tables (Appendix A) and include the samples collected at similar sites from all of the plants surveyed. Results of analyses of samples are grouped for similar operations to show the minimum, maximum, median and average atmospheric concentrations in the various areas. Those plants having operations or processes differing from the majority of the companies or which would identify individual plants, will receive a separate report of the findings for these particular operations.

Dry Mill

Fourteen samples, including concentrated ore, settled dust, and air-borne dust from various areas, showed a free silica content well below 5 percent. Based on these results it may be concluded that exposure to these dusts would not constitute a silicosis hazard provided daily weighted exposures did not exceed the threshold limit value (TLV) of 50 million particles per cubic foot of air (mpcf).

Dust concentrations, shown in Table 1, were generally low at drying and grinding operations. However, they were exceedingly high at storage and shipping where nearly 90 percent of the samples collected exceeded the TLV. Maximum dust values were over 23,700 mpcf in the storage area and 693 mpcf in shipping. The median particle size of the air-borne dust in the dry mill area, collected on membrane filters and determined by electron microscopy, ranged from 0.1 to 0.3 micron in diameter. Dust concentrations obtained, using the technique described in Appendix B, and reported in Table 1, include only those particles in the size range from about 1 to 5 microns, the range upon which TLV's are based.

Fluoride concentrations of air-borne dust are shown in Table 2. As indicated, fluoride levels at drying and grinding operations are reasonably low and within the TLV of 2.5 milligrams of fluoride per cubic meter of air (mg F/m^3). However, 70 percent of the samples collected at storage and 30 percent at shipping exceeded the TLV for fluoride. Maximum concentrations in the storage area were 92 mg F/m^3, and at shipping were 41 mg F/m^3.

Spectrographic analyses of metallic and metal-like elements were made on samples of dried concentrated ore and dried, ground, concentrated ore collected in one dry mill. The results are shown in Table 3. Calcium and phosphorus are the major constituents with silicon, iron, magnesium, aluminum and manganese present as minor constituents (less than 1 percent). Minute amounts of lead, tin, sodium, chromium, vanadium, titanium, and trace amounts of nickel, barium, and beryllium were found.

Uranium was not detectable under conditions of the spectrographic method employed. Small amounts of uranium in bulk samples would have to be concentrated chemically to make spectrographic detection possible. Although uranium provides many hundreds of lines in its emission spectrum, its lines are much weaker than those of the more common heavy metals. This explains why low concentrations of this element are difficult or impossible to detect by direct spectrographic examinations, such as were employed in the analysis of these samples.

Chemical Plant

The principal hazard at car unloading was dust. This operation was observed visually to be very dusty and only a few samples were needed for confirmation. Two of the three dust counts made at car unloading (Table 1) greatly exceeded the TLV of 50 mpcf for nuisance dusts and 40 percent of the air-borne samples for fluoride exceeded the TLV of 2.5 mg F/m^3 (Table 2).

Not all of the chemical plants operated grinders. Those which were observed did not appear to be dusty and the few samples collected for dust counts and fluoride analysis were well below the TLV.

Acid mists were the primary exposure at filtration operations. Although 13 percent of the samples (Table 2) exceeded 2.5 mg F/m^3, median and average values were well below this level. Air-borne concentrations of phosphates, expressed as phosphoric acid, and sulfates as sulfuric acid are shown in Table 4. It is difficult to interpret these levels because of the presence of dusts containing phosphates and sulfates. It is believed, however, that the greater portion existed as acid mists because the higher concentrations were associated with eye, nose and throat irritation which at times exceeded comfort levels.

At acidulation, acid mixing, curing and storage, and shipping operations there were exposures to gaseous (probably HF) and particulate fluorides as well as to sulfates and phosphates, some of which were probably in their acid form. Of the 126 samples collected in these areas for fluorides (gaseous and particulate combined, Table 2), 50 percent exceeded the TLV of 2.5 mg F/m^3. Maximum concentrations ranged from 9.5 to 144 mg F/m^3. Maximum concentrations of phosphoric acid (Table 4) ranged from 2.9 to 17.0 mg/m^3 and sulfuric acid from 0.8 to 14.0 mg/m^3. As stated previously, interpretation of these results is difficult. The higher concentrations were associated with severe eye, nose and throat irritation and definitely exceeded comfort levels.

Dust counts in the curing and storage and shipping areas (Table 1) ranged from 133 to 443 mpcf (maximum values) with around 15 percent exceeding the TLV of 50 mpcf.

Urine Levels

Urine fluoride levels were determined on members of the survey team. Samples were collected during the first and last days of the survey and, on three members of the team, two months after the survey was completed.

Results are shown in Table 5. Past studies have shown that excretion of fluoride in the urine is an indication of fluoride absorption and consequently of fluoride exposures. In interpreting these results it should be pointed out that the survey team intentionally did not wear respirators except when essential. Thus their exposure to fluorides may have been higher than that of a worker who effectively used a respirator. On the other hand, the survey team covered a large area during any one day's sampling and would not remain as long in a high level area as a worker whose duties required his presence in that area. Nevertheless, during the survey the urine fluoride values of the team showed a marked increase over normal levels.

Discussion of Results

Dry Mill

The dust in the dry mill area was well under 5 percent in free silica content. No silicosis hazard would be probable in this area providing exposure levels are kept at or below the TLV of 50 mpcf.

Fluoride concentrations of air-borne dust at storage and shipping operations at times considerably exceeded the TLV of 2.5 mg F/m^3. It must be kept in mind that the concentrations shown in Table 2 were not weighted exposure levels of workers. They were cross-section samples to determine levels of concentrations at various operations.

There is very limited information in the literature on interpreting exposures to phosphate rock dust in terms of any inherent fluoride hazard. Since urine fluoride excretion is an indication of fluoride absorption and exposure, urine fluoride levels on workers in this area would be invaluable. There is also a need for additional clinical information relative to fluoride exposures of the workers. Information of this nature must be obtained before an evaluation can be made on the extent of any fluoride hazard from phosphate rock dust.

Chemical Plant

In the chemical plant there were potential health hazards to phosphate rock dust, gaseous and particulate fluorides, and phosphates and sulfates probably in their acid form.

The greatest dust problem was at the car unloading operation. The same factors and considerations to dust exposures in the dry mill apply here.

Exposure to gaseous and particulate fluorides was widespread in the chemical plant. Over half of the atmospheric fluoride concentrations exceeded the TLV of 2.5 mg F/m^3. Maximum concentrations were also at times extremely high. These were not weighted exposures and do not take into consideration any personal respiratory protection. However, it was observed that respirators were used only at a few operations in each plant. At these locations respirators were not worn by all workers. Information on urine fluoride levels on workers in this area and other clinical data indicative of fluoride absorption would be invaluable. The urine fluoride levels of the survey team indicates the definite need for this information.

Since the higher levels of phosphates and sulfates, expressed as acids, were associated with eye, nose and throat irritation, it would be desirable for the plants to determine the exact chemical nature of these substances. It is quite likely that the hydrogen fluoride present added to, or was the principal cause of, the irritation and discomfort noted.

Summary and Recommendations

An industrial hygiene survey was conducted in the phosphate plant located in Polk County, Florida during May-June and October-November 1957 by the Occupational Health Program, U. S. Public Health Service and the Industrial Hygiene Division, Florida State Board of Health. In general the information collected during the preliminary survey and the subsequent environmental sampling survey indicated potential problems in several plant areas from exposures to dusts, gaseous and particulate fluorides, and acid phosphates and sulfates. Some work areas had extremely high concentrations of dusts and fluorides, both gaseous and particulate. Even though these exposures are, in some instances, brief and intermittent, management should study these operations and assure adequate protection of the worker. It is recommended that environmental and medical studies be conducted in this industry to define the extent and magnitude of these potential health hazards. These studies should include:

(1) Routine air sampling to determine the weighted exposures to the various contaminants encountered.

(2) Routine urine fluoride analyses on workers in the dry mill and chemical plant areas.

(3) Physical examinations of workers. The scope of these examinations should be extended to detect changes which might result from exposure to toxic materials encountered in the working environment.

The Florida State Department of Health and Public Health Service will be glad to assist in the planning and conduct of these studies.

Appendix A

Table 1. Air-borne dust concentrations in plants studied by area or operation

Area or Operation*	No. of Samples	Dust concentration in millions of particles per cubic foot of air (mpcf)			Percent of samples Above TLV**
		Range	Median	Average	
Dry Mill					
Drying	6	0.8 - 108	19.6	33	16.7
Grinding	3	7 - 37	22.0	22	0
Storage	13	41 - 23,700	930	3,760	92.5
Shipping	7	7 - 693	450	342	85.6
Chemical Plant					
Car unloading	3	14 - 2,180	152	782	66.6
Grinding	1	19	-	-	0
Curing & storage	3	3 - 133	4	49.3	33.3
Shipping	7	4 - 443	19	76.5	14.3

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* See Appendix B for more detailed explanation of sampling areas.

** The Threshold Limit Value for nuisance dusts, those containing less than 5 percent free silica, is 50 mpcf.

Table 2. Concentration of air-borne fluorides in plants studied by area or operation

Area or Operation*	No. of Samples	Concentration of fluorides expressed as F mg/m^3 **			Percent of samples above TLV**
		Range	Median	Average	
Dry Mill					
Drying	16	0 - 1.7	0.2	0.4	0
Grinding	18	0.03 - 8.3	0.2	0.9	6
Storage	23	0.3 - 92	4.4	12.4	70
Shipping	27	0.05 - 41	1.3	4.4	30
Chemical Plant					
Car unloading	5	0.1 - 12.5	0.6	3.4	40
Grinding	6	0.1 - 2.5	0.5	0.8	0
Acidulation	26	0.4 - 9.5	2.4	3.2	50
Filtration	23	0.1 - 3.9	1.1	1.3	13
Acid mixing	23	0.3 - 20.3	2.5	4.5	48
Curing & Storage	49	0.6 -144	4.9	14.8	69
Shipping	28	0.1 - 11	0.6	2.1	25

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* See Appendix B for more detailed explanation of sampling locations.

** Threshold Limit Values adopted in April 1957 by the American Conference of Governmental Industrial Hygienists. The value for fluorides as gas (HF) and dust (F) is 2.5 milligrams per cubic meter of air (mg/m^3).

Table 3. Spectrographic analyses of phosphate ore from one plant.

Description	Dried Concentrated Phosphate Ore	Dried Ground Concentrate
Element	(Micrograms per gram or parts per million)	
Ca P	Major Constituents	Major Constituents
Fe	1,300	1,300
Mg	1,200	1,200
Al	620	620
Mn	600	600
Si Na	Minor Constituents	Minor Constituents
Pb	100	50
Sn	120	120
Ba	120	120
Cr	50	50
V	30	30
Co	1	n. d.*
Ni	5	2
Be	2	1

* None detectable.

Antimony, arsenic, bismuth, boron, cadmium, germanium, mercury, tellurium, and uranium were not detected.

Table 4. Concentration of air-borne phosphates and sulfates in plants studied by area or operation.

Area or * peration	No. of Samples	Phosphates expressed as $mg/m^3 H_3PO_4$**			No. of Samples	Sulfates expressed as $mg/m^3 H_2SO_4$**		
		Range	Median	Average		Range	Median	Average
hemical Plant								
cidulation	19	0 - 2.9	0.9	1.0	20	0 - 8.4	1.0	1.7
iltration	22	0 - 2.1	0.6	0.7	22	0 - 6.2	1.5	1.7
id mixing	11	0.7 - 3.5	1.3	1.7	9	0.2 - 5.4	0.9	1.6
uring and Storage	16	0 - 17.0	1.1	2.9	16	0 - 14	1.0	3.0
hipping	2	11.2 - 13.8	12.4	12.4	2	0.6 - 0.8	0.7	0.7

* See Appendix B for more detailed explanation of sampling locations.

** These values include phosphoric and sulfuric acid mists and dust containing phosphates and sulfates.

Table 5. Fluoride urine levels of survey team.

Surveyor	Date collected	Total milligrams fluoride per 24 hours	Milligrams fluoride per liter per 24 hours
A	10/16/17-57	3.0	1.5
B	10/16/17-57	3.1	1.3
C	10/16/17-57	1.0	1.2
D	10/16/17-57	2.6	2.0
E	10/16/17-57	2.3	2.1
A	11/7/8-57	7.5	5.5
B	11/7/8-57	11.3	3.4
C	11/7/8-57	6.7	3.2
D	11/7/8-57	6.4	5.5
E	11/7/8-57	2.5	1.9
A	1/14/15-58	0.9	0.5
B	1/14/15-58	1.6	0.5
C	1/14/15-58	0.8	0.5

Appendix B

Sampling Locations

As previously mentioned, information was obtained and observations were made during the preliminary survey on the various processing and manufacturing operations. From this data sites were selected for collection. Furthermore, since this survey covered all plants in Polk County, an attempt was made to select sampling locations which would be representative in the majority of plants surveyed. The following general locations were chosen:

A. Drying, grinding, storing and shipping phosphate rock.
   1. Dryer area--usually near control panel where operator spends most of the time. In addition, general room air samples were collected in the dryer area at several plants.
   2. Grinding area--usually near control panel, also general air samples in several plants.
   3. Storage area--beside transfer belt above storage silos and also in screen area in most plants.
   4. Shipping--hopper and/or box car loading; and, in a few plants, loading trucks.

B. Chemical plants (manufacture of superphosphate and triple superphosphate).
   1. Car unloading of dried, ground phosphate rock. Samples were usually collected at operators' breathing zone and represent maximum exposures in most instances.
   2. Acidulation--addition of sulfuric acid to phosphate rock to produce either phosphoric acid or superphosphate depending

upon the type of product desired. Samples were usually collected to represent the operators' normal exposure and the exact location was varied depending upon the particular plant design.

3. Filter area--separation of dilute phosphoric acid from sludge (principally calcium sulfate). Exact locations varied depending upon type of filters used but in general would represent the operators' average exposure.
4. Mixing phosphoric acid and phosphate rock to produce triple superphosphate--samples were collected at the point where these two materials were mixed and also in the vicinity of the discharge end of the equipment. Naturally, the exact location was different from plant to plant depending upon the type of equipment in use.
5. Curing and storage--locations included the conveyor belt from 4. above to the storage area and conveyor belt above storage sheds in most plants. An attempt was made to collect air samples at those locations where operators spend a portion of their time.
6. Shipping--locations included removal of product from storage area, whether by shovel, payloader, overhead crane, or other methods; at grinding and/or screen operations, where employed; and loading--hopper car, box car, truck or bagging, whichever methods were employed.

C. Miscellaneous locations--those not common to all plants.

Methods of Sampling

Standard field sampling equipment was used for the collection of all air samples. This equipment was calibrated for air flow in the laboratory prior to the survey and after the instruments were returned to Cincinnati. The following types of instruments were used and the approximate sampling rate is stated in parentheses:

(1) Midget impinger and pump--for dust counts and some particle size determinations (0.1 cubic foot per minute, cfm).

(2) Greenburg-Smith impinger--for fluoride concentrations both gaseous and particulate, for acid mists--phosphoric, sulfuric and hydrofluoric, and for other special analyses (1.0 cfm).

(3) Membrane Filter (Millipore type AA) with 1 inch effective diameter in special holder. Source of suction was Gast, Denver or Midget impinger pumps depending upon conditions and availability of electric power--for collection of particulates for various chemical, spectrographic and x-ray diffraction analyses and particle size determination by the electronmicroscope (sampling rate varied with source of suction used from 3 to about 15 liters per minute).

(4) A membrane filter in series with a Greenburg-Smith impinger was used to separate particulate and gaseous fluorides (15 liters per minute).

(5) Fritted glass bubblers using benzene as the collecting solution, either alone or preceded by a membrane filter--for collection of special samples at one elemental phosphorus plant (about 10 liters per minute).

(6) National Bureau of Standards Carbon Monoxide Detector--for determining concentrations of carbon monoxide in selected locations.

The collection efficiency of these instruments has been checked by various investigators and is at least 95 percent efficient for the kinds of samples collected during this survey. The midget impinger, the efficiency of which falls off rapidly as the particle size decreases below 1 micron, is the single exception to this statement.

A few selected 24-hour urine samples were collected in Pyrex bottles with 5 ml. 15 percent formaldehyde added as a preservative. These samples were collected from all members of the survey team on October 16, the first day of their plant exposures, and on November 12, the last day.

Methods of Analysis

1. Dust counts were made by the light-field counting techniques using a binocular microscope with 10X eyepieces and 10X objective. The counting cell used was the Spencer Brightline Haemocytometer as described by Charles R. Williams.(1)

2. Particle size determinations from impinger samples were made by placing a drop of dust suspension on a microscope slide, evaporating the liquid, adding a drop of DuCo cement and covering with a cover slip. The diameters of at least 200 particles were measured using a 97X oil immersion objective, 10X eyepiece with a Mays (Porton) eyepiece graticule, and under Kohler illumination.

3. Particle size determinations by the electromicroscope were made according to a method developed by Fraser.(2) Briefly, a small section of membrane filter is placed, dust side down, on an electronmicroscope

grid which in turn is placed on a supporting wire screen in a Petri dish. Ethyl acetate is carefully added to the wire screen level and by capillary attraction the membrane filter is dissolved leaving the dust deposited on the grid (previously coated with Formvar). Selected portions of the grid are photographed at a magnification of about 9,000X. The diameters of at least 150 particles are estimated by projecting the negative onto a screen and comparison with a ruled grid (calibrated for the particular projected magnification).

4. Determination of Fluoride in Urine (Modification of Smith and Gardner(3)). Sample is thoroughly mixed and transferred to a graduated cylinder for volume measurement. Any precipitate remaining in sample bottle is removed with 1:1 acetic acid, double distilled water and a policeman (rubber) if necessary. All volumes are recorded. The precipitate, washings and urine are recombined and thoroughly mixed. A 25 ml. aliquot (graduated cylinder) is transferred to a platinum dish containing 0.8 g. (low in fluoride) CaO, stirred and checked for alkalinity with litmus paper. If not alkaline additional CaO is added. Total CaO is recorded for blank correction.

Aliquot is evaporated to dryness, charred and finally ashed at 575 °C until a white or near white ash is obtained. The ash is transferred to a fluoride still and steam distilled from 35 ml of 70 percent $HClO_4$ according to the Winter and Willard procedure,(4) collecting 225 ml of distillate in a 250 ml volumetric flask. Distillate is diluted to the mark and suitable aliquot is taken for colorimetric determination of fluoride with thorium-alizarin reagents.(5)

5. Determination of fluoride in air--Greenburg-Smith impinger samples collected in 0.1N NaOH. Transfer entire sample, after recording the volume, to a platinum dish. Make sure solution is alkaline (litmus). Evaporate to dryness, or a small volume, and transfer quantitatively to a fluoride still. Steam distill from 35 ml of 70 percent $HClO_4$ according to Winter and Willard procedure.(4) Collect 225 ml of distillate in a 250 ml volumetric flask. Dilute to mark and take a suitable aliquot for colorimetric determination with thorium-alizarin reagents.(5)

6. Determination of fluoride in air--membrane filter samples (transported in envelopes to laboratory). Transfer filter and loose dust of sample to a platinum crucible, add 0.1 gram CaO (low in fluoride) and sufficient double distilled water (4 to 5 ml) to wet the filter thoroughly. Evaporate to dryness, swirling occasionally to maintain intimate contact between the filter and the lime, and then ash at 575 °C in a muffle furnace for two hours. Cool, wash down the walls of the crucible with 4 to 5 ml double distilled water, stir with a platinum spatula to break up the residue, evaporate to dryness (swirl occasionally) and dry ash for one hour at the same temperature as before. The residue should be white or greyish-white. Make a slurry of the ash with water and transfer to a fluoride still. Add about 2 ml of water and then 0.5 ml $HClO_4$ to the crucible and then stir with a platinum spatula, rubbing entire inner surface of crucible to effect a quantitative transfer of residual ash to the still. Add 35 ml of 70 percent $HClO_4$ and apply distillation and estimation procedures outlined above for the impinger samples.

A group of unused filters from the same batch as those used for the samples was carried through the entire procedure to provide a reliable blank value. This value was applied in all determinations.

7. Determination of Sulfates in Acid Mist Samples (Modification of Eschka Method(6)).

1. Take 10 ml portion of sample solution (or 10 ml of 0.1N NaOH for standard series).
2. Acidify with 1:4 HCl; add bromcresol green indicator and adjust pH to 4.0 (yellow side) with 1N HCl.
3. Add 5 ml of 1:2 glycerin--alcohol mixture.
4. Dilute to 25 ml with distilled water in graduated cylinder. Mix.
5. Add one scoop (0.25 gram) of barium chloride (low in sulfate) and mix until salt is dissolved.
6. Allow to stand for 40 minutes, mix well and transfer to matched test tube.
7. Read percent transmittance at 500 m μ, with Beckman DU spectrophotometer, with the slit set at 0.03 mm.

8. Determination of Phosphates in Acid Mist Samples (Modification of Kitson and Mellon Method(7)).

1. Transfer 10 ml or more of sample solution (or the same amount of 0.1N NaOH for standard series) to a 125 ml Phillips beaker.
2. Neutralize with 1:2 HNO_3 and add 10 ml excess, cover and heat to boiling. Boil 2 minutes.
3. Add 5 ml freshly prepared 7.5 percent solution of ammonium peroxydisulfate (persulfate), boil 3 to 5 minutes, covered.

4. Add 10 ml of 0.25 percent ammonium vanadate to the hot solution.
5. Cool to room temperature.
6. Add 20 ml of 5 percent ammonium molybdate solution and mix.
7. Transfer to 100 ml graduate and dilute to mark. Mix thoroughly.
8. Transfer to matched test tubes and let stand 30 minutes.
9. Measure percent transmittance at 470 mμ with a slit of 0.04 mm (with Beckman DU spectrophotometer), Cell "Out," against a reagent blank as reference.

9. Method for the Determination of Elemental Phosphorus--Transfer the benzene solution of the sample to a separatory funnel. Shake vigorously for 1 minute with 25 ml of cooled, freshly-boiled, double distilled water. Let the layers separate and draw off the aqueous layer. If large amount of oxides are present, repeat using about 15 ml of water.

To the benzene layer add 10 ml of 1 percent $AgNO_3$ and shake vigorously for 2 minutes. Elemental phosphorus will give a black precipitate or darkening in the $AgNO_3$ layer at this point. A few micrograms of P will be noticeable. Add 10 ml concentrated HNO_3 with swirling and immediately shake for 2 minutes. Allow layers to separate and draw off the aqueous layer into a clean 100 ml beaker. Add 10 ml 1:1 HNO_3 to the benzene and repeat the shaking. Draw off the HNO_3 layer into the same beaker. Repeat the last treatment using 5 to 10 ml 1:1 HNO. Discard the benzene layer.

Heat the nitric acid solution on the water bath until residual amounts of benzene have been vaporized. Precipitate Ag as AgCl by adding 10 ml 1:3 HCl, filter, and wash with 1 percent HCl. Discard precipitate, evaporate filtrate to small volume to remove excess HCl, and boil with ammonium peroxydisulfate to destroy organic matter.

Determine phosphate concentration by procedure of Kitson and Mellon.(7)

10. Free silica determinations on bulk sample materials were performed by a phosphoric acid method(8) after a preliminary treatment with boric acid and perchloric acid to remove fluorine.

11. Spectrographic analyses were made using a Bausch and Lomb large Littrow spectrograph, with quartz optics, and a 220 volt d.c. arc for excitation. Spectroscopically pure graphite electrodes were used. A 3 mm crater in the anode supported a mixture of 5 mg of lithium chloride-graphite spectroscopic buffer(9) and 5 mg of ground, bulk sample material. Arcing of this mixture was conducted to lithium chloride burn-out with the arc focused on the slit of the spectrograph and the spectra were recorded on an Eastman Kodak III - 0 spectroscopic emulsion in the 2100 - 3300 A region and a III - F emulsion in the 3300 - 6000 A region. The plates were developed and fixed at 68 °F. Semiquantitative estimations of element concentrations were made using a Jarrell-Ash Model 200 Comparator Densitometer and visual standards.(10)

All analytical methods, with the exception of that for elemental phosphorus, were checked by recovery determinations of known amounts of added analysis elements. For the evaluation of the method used in the analysis of fluoride collected on filter media, known amounts of fluoride (as NaF) were added to filters from the same batch used in the survey. One hundred percent recovery was obtained when these were analyzed by the described procedure.

Analytical blanks were established for all methods used in the survey. These blanks, based upon the sampling media, laboratory reagents, glassware, etc., provided correction factors applied to the respective determinations.

Field blank samples submitted by the survey team, unknown to the analyst, were processed along with the regular samples. These served as both sampling and analysis checks in this survey.

References to Analytical Methods

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