INDUSTRIAL HYGIENE SURVEY

OF

Agrico Chemical Company

SURVEY DATE

June 22-26, 1975

SURVEY CONDUCTED BY

Melvin E. Cassady
Harry Donaldson
Steven Gentry

REPORT WRITTEN BY

Melvin E. Cassady

DATE OF REPORT

Industrial Hygiene Section
Division of Surveillance, Hazard Evaluations and Field Studies
National Institute for Occupational Safety and Health
Cincinnati, Ohio

PLACE VISITED:	Agrico Chemical Company-South Pierce Chemical Works Pierce, Florida (813) 428-1431 Agrico Chemical Company Pierce, Florida (813) 428-1431
DATE OF VISIT:	June 22-26, 1975
PERSONS CONTACTED:	Mr. J. Weathers, Safety Engineer, Agrico, South Pierce Complex M. Johnson, Environmental Chemist Agrico, South Pierce Complex C.A. Nicholson, Environmental Control Superintendent K. Midbow, Assistant Manager, Ind. Relations
PURPOSE OF VISIT:	To collect environmental data on exposure of personnel to H_2SO_4, H_3PO_4, Cr, U, fluorides and radiation during the cleaning of the H_3PO_4 reactor vessels.

INTRODUCTION

The Division of Surveillance, Hazard Evaluation, and Field Studies (DSHEFS), of the National Institute for Occupational Safety and Health (NIOSH), was requested to investigate the environmental conditions at a wet chemical fertilizer plant where three persons working on the same job and alledged non-smokers were diagnosed as having lung cancer.

During October, 1974, a team of investigators for DSHEFS toured the plant located in Polk County, Florida, where the three lung cancers were reported. On May 12, 1975, as a follow-up to the October 1974 walk-through survey, and to determine if there were any variations in other facilities having wet chemical operations, Messrs. David Bayliss, Gordon Nifong, and Melvin Cassady performed a walk-through survey of several wet chemical plants located in Polk County, Florida, including Agrico Chemical Company's facility.

DESCRIPTION OF PHOSPHATE FERTILIZER MANUFACTURING

The following is a narative description of the process of manufacturing phosphate fertilizer. The appendix gives a schematic of the process. The first step in the mining of phosphate rock is the removal of the overburden, which consists generally of sand and sandy clay. The overburden is removed using large dragline excavators.

Once the overburden (waste) has been removed and dumped into adjacent mined out areas, the dragline excavates the phosphate bearing ore (matrix). The matrix is dumped into a shallow pit located adjacent to the mining cut then slurried with high pressure streams of water from hydraulically operated guns.

The slurry is pumped to the beneficiation plant where it is washed, sized crushed and floated to remove silica and other impurities; the resulting product is a pebble phosphate rock consisting of two sizes -- coarse rock which runs minus 3/4 inch plus six mesh and regular rock which runs minus six plus 4 mesh.

From the beneficiation plant the phosphate rock is shipped to a drying and storage plant where it is dried and then stored for subsequent shipment to the chemical plant.

The chemical plant utilizes molten sulfur as a raw material to manufacture sulfuric acid by the conventional Contact Sulfuric Acid Process. In this operation elemental sulfur is burned in a combustion chamber to form sulfur dioxide gas which is then passed through a series of converters, charged with catalyst and then interacted with air to form sulfur trioxide gas which is in turn passed on to the absorption tower, where it is interacted

with water and weak sulfuric acid to form a strong sulfuric acid. Phosphate rock is received, ground and mixed with sulfuric acid to produce phosphoric acid. The reaction is $Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 2\ HF + 6H_3PO_4$. The HF formed in this reaction reacts with SiO_2 to form the hydrofluorosilicic acid (H_2SiF_6).

DESCRIPTION OF PLANT

Agrico Chemical Company's South Pierce Chemical Complex has been in operation since 1964; and the Mining Division since the early 1900's. The chemical complex consists of six main operating units: crushing and grinding; sulfuric acid plant; phosphoric acid plant; triple superphosphate production facility; mono and diammonium phosphate; and storage and drying areas.

The total work force of the South Pierce Chemical Complex consists of approximately 385 persons of which 271 are hourly workers; the Mining division consists of a total of 1072 persons of which 802 are hourly workers. The production workers are represented by the International Chemical Workers Union.

The plant operates three shifts per day, seven days per week producing phosphoric acid (54% P_2O_5), triple superphosphate, and fluorosilicic salts and acids as the major products.

MEDICAL, SAFETY AND INDUSTRIAL HYGIENE PROGRAM

This facility does not have inplant medical facilities. The General Practice Clinic in Lakeland, Florida, is retained to perform the pre-employment physical exams and other emergency care. While there is no full time nurse at the plant, several persons have been certified in energency medical training.

The pre-employment physical examination consists of a medical history, eye examination, hearing test, and x-rays for chest and lower back. The primary concern seems to be that of back problems.

The safety program consists of accident prevention with no systematic approach or incentive award program. Agrico has one full time safety engineer for the South Pierce Chemical Complex. When accidents occur they are investigated by a safety committee consisting of 2 union personnel and the safety engineer. The employees are provided with safety glasses and hard hats and are required to wear safety shoes which are purchased at their own expense. Respiratory protective equipment consists of Scott Air Pac, White Cap units, half mask respirators with acid gas cartridges and disposable dust respirators for nuisance dust. No respirators were observed being used during the walk-through survey.

This facility does not presently employ an industrial hygienist but relies on outside consultants for this expertise.

The ventilation systems are primarily process units or air pollution control devices, however, they are effective in controlling dust at major areas where considerable dust may be generated. Baghouses and cyclones are used as classifiers on process units and wet scrubbers are used for control of fluorides.

POTENTIAL HEALTH HAZARDS

The major potential health hazards observed during this survey are the following:

Sulfuric Acid Plant

Asbestos -- Asbestos is used as an insulative material for all steam lines in the contact acid plant area. Exposure could occur during insulation repair or replacement operations.

Sulfur Dioxide -- Overall the concentration of sulfur dioxide was very low except for instances of leaks in the gas handling systems when excessive exposure could occur.

Sulfuric Acid Mist -- Exposure to sulfuric acid mist in this area could result from poor maintenance of the gas handling systems or from upsets in the acid plant operation.

Vandium Pentoxide -- Vandium pentoxide (V_2O_5) is used as a catalyst in the acid plant operation. Exposure to V_2O_5 dust could occur while changing or raking the catalyst bed.

Milling

Dust -- The potential exists for dust being generated at the ore pocket while phosphate rock is being dumped from rail cars; during classification (sizing) operations or screening; during the batch weighing of phosphate rock for the phosphoric acid reactor. (The batch weighing process appears to be completely automated. No personnel were observed in the area during the walk-through survey.)

Phosphoric Acid Plant

Phosphoric Acid Mists -- Considerable phosphoric acid mists and

droplets could be generated in the production of phosphoric acid from phosphate rock and sulfuric or through material handling.

Sulfuric Acid Mist -- Sulfuric acid is used as a reactant therefore a mist could be generated in the phosphoric reaction vessel.

Fluorides -- The phosphate ore contains 3-5% fluoride. During the chemical processing of phosphate rock with sulfuric acid, the fluorides are liberated as hydrofluorosilic acid.

Uranium -- Uranium and its decay products are found in the phosphate deposits in Central Florida. Virtually all the uranium remains with the fertilizer, while a major portion of the radium and subsequent decay products are removed in the liquid and solids wastes.[1]

ENVIRONMENTAL SURVEY

The operation evaluated by NIOSH was the cleaning of a large phosphoric acid reactor vessel. During the study 8-hour time weighted averages samples for cadmium, chromium, vanadium, phosphoric acid and sulfuric acid were collected on workers involved in cleaning out the reactor vessel. In addition to the personal samples, general area samples were collected for fluorides.

Heavy Metals

Heavy metal samples were collected at a flow rate of 2.0 lpm by a dampened MSA Model G sampling pump using 37mm AA Millipore filter, 0.8 micron pore size, as a collection media. The sampling duration varied from 4 to 8 hours. The analysis was done using atomic absorption spectroscopy.

Sulfuric Acid Mist

Sulfuric acid mist samples were collected at a flow rate of 2.0 lpm by a dampened MSA Model G sampling pump using 37mm, 0.8 micron pore size, AA Millipore filter, as a collection media. The sampling duration varied from 4 to 8 hours. The sulfuric acid mist was analyzed using a titration method for the sulfate ion.

Phosphoric Acid Mist

Phosphoric acid mist samples were collected at a flow rate of 2.0 lpm by a dampened MSA Model G sampling pump using 37mm AA Millipore filters, 0.8 micron pore size, as a collection media. The sampling duration varied from 4 to 8 hours. The phosphoric acid was analyzed using heteropolyblue colorimetric method.

Fluoride

Fluoride samples were collected at a flow rate of 2.0 lpm using a dampened MSA Model G sampling pump and midget impinger containing 10 milliliters (ml) of 0.1M sodium acetate. The impinger was preceeded by a 35mm AA Millipore filter to collect the particulate fluorides. The fluoride determination was done using a specific ion electrode with a 1:1 solution of fluoride and total ionic strength activity buffer.

Radon

The radon sampling was performed by the EPA's radiation protection team.

Uranium

The uranium particulate sampling and beta radiation levels were evaluated by EPA's radiation protection team.

CURRENT WORK PRACTICES

The tank is emptied of all phosphoric acid then flushed with water several times over a period of 24-48 hours. High volume air movers are then attached to openings on the top of the reactor tank and the system is purged with air. Prior to tank entry the oxygen content is checked.

Personnel are provided with high top rubber boots, rubber gloves, safety glasses, and rain or acid resistant rubberized suits. A water hose is placed in the tank to furnish water in the event acid gets on the skin or in the eyes. Several people work in the reactor vessel at the same time with observers stationed on the outside of the tank.

The cleaning procedures consists of chipping away at the gypsum deposited on the agitator, flash coolers, and sidewalls of the reactor. Manual and pneumatic equipment is used in the procedure.

The gypsum is put in wheelbarrows and dumped at an opening where it is mucked out and deposited on the ground. This procedure takes anywhere from 3 to 5 days to complete.

One major problem encountered during the cleaning procedure was that during the period while people were in the tank chipping away the gypsum material from the sidewalls, people were also chipping away material deposited at the upper openings. A large amount of debris was broken loose at one point and fell on personnel working below. This created a dangerous situation where people were subjected to not only the impact of falling debris but the potential for splashing of chemicals in the eye or otherwise introductions of foreign material in the eye.

RESULTS AND DISCUSSION

Table I gives the range of concentration as well as the standard for the contaminants. The individual sample results are tabulated in Table II.

Table I

Environmental Data

Contaminant	High	Low	Standard
Fluoride (particulate)	0.189	0.071	25 mg/m^3
Fluoride (gaseous)	0.676	0.068	
Phosphoric Acid	0.118	0.005	1.0 mg/m^3
Cadmium (dust)	0.001	--	0.2 mg/m^3
Chromium	0.003	0.001	1.0 mg/m^3
Vanadium (dust)	0.009	--	0.5 mg/m^3
Sulfuric Acid	0.070	--	1.0 mg/m^3

As can be noted in Table I, all contaminants were below the current legal standard.

EPA was responsible for providing the data and discussion of the radiation exposure to personnel involved in the clean-out operation. A report specially dealing with that area is suppose to be forthcoming from EPA.

RECOMMENDATION

One major problem encountered during the cleaning procedure was that during the period while people were in the tank chipping away the gypsum deposits from the sidewalls people were also chipping away material deposits at the upper openings. It is recommended that no one loosens debris at the top of the tank while personnel are working inside the tank.

It is also recommended that approved respiratory protection for acid mist continue to be worn while working in the reactor to protect the worker against the irritation effect of the acid mists. Also it is recommended that the use of splash goggles and protective clothing be encouraged to provide adequate protection to skin and eyes. Portable eye baths should be placed in the immediate area where work is being performed.

Agrico's facility is not suitable for study because the latency period is too short and also the medical and personnel records were not adequate to perform a retrospective mortality study. The reason for inadequate records was that all but the last 5 years were destroyed. Current regulations do not require keeping records for more than 5 years.