LEAD INDUSTRIES ASSOCIATION

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NEW YORK 17, N. Y.

METALLIC LEAD PRODUCTS DIVISION

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1. SUMMARY

The manufacture of phosphoric acid is an integral part of the production of phosphate fertilizers. Manufacturing phosphoric acid from phosphate rock involves corrosive conditions which are best met through the use of lead protected equipment. Comparative corrosion data on lead and several types of stainless steel indicated that lead is a most practical material to use in processing equipment due both to its excellent corrosion resistance and the fact that it is economical to install and maintain.

2. LOCATION

Phosphate Plant, The Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C.

3. PROCESS

Phosphate rock as mined is crushed and wet-ground in pebble mills in the presence of phosphoric acid. The mill discharge together with dry, fine ground phosphate rock is reacted in five agitators in series. Sulphuric acid is fed to the last two agitators. Slurry is recirculated from these two agitators to the head of the circuit. Conditions of temperature, free sulphuric acid and phosphorus pentoxide (phosphoric acid) are carefully controlled in the agitator to produce readily filterable gypsum ($CaSO_4 \cdot 2\ H_2O$). After the gypsum is filtered off, repulping, agitation and filtration follow in two successive stages with counter-current washing of gypsum on the filter. Production acid averages 32 to 33 percent phosphorus pentoxide (about 45 percent phosphoric acid) and washed gypsum contains about 1 percent phosphorus pentoxide. A flow diagram of the process accompanies this bulletin.

4. CONSTRUCTION DETAILS

The Phosphate Plant was designed by the Dorr Company, Inc., New York, N. Y., the patentee of these processes. Construction details of those units in which lead is used are indicated below.

A. Reaction Agitators and Air Coolers

All agitators of the first stage circuit consist of tanks approximately 12 ft. 6 in. in diameter by 11 ft. in height constructed either of wood lined with 10-lb. hard sheet lead (5 to 6 percent antimony) and Duro brick, or 10-lb. hard lead, brick lined, with a supporting skeleton of steel bands on the outside. The covers are 3 in. wood decking. The agitators are interconnected at the top by hard lead launders and each is equipped with AISI type 316 stainless steel shaft and propeller driven through "tex" pulleys. Two air cooling boxes constructed of heavy hard lead plate are submerged under several inches of slurry in each of the latter three agitators of the first stage circuit. Air is blown into these boxes and through the slurry to control the temperature of the slurry by evaporation cooling.

Second and third stage reaction agitators are of similar size and construction as the repulp agitators.

B. Repulp Agitators

The repulp agitators serve to mix the gypsum cake with filtrate phosphoric acid to produce a pulp which can be readily pumped into the agitators of the second or third stage reaction circuits. Retention time is approximately 20 min. These units are 12 ft. 6 in. in diameter by 11 ft. high of wood stave construction and lined with hard lead sheet and Duro acid proof brick. Agitation is provided by a 20 h.p. motor with stainless steel agitator shaft and propellers similar to the equipment used in the reaction agitator. The pulp from the first stage repulp agitator averages 38 percent solids by weight, 20 percent phosphoric acid and 2.5 percent sulphuric acid, while that from the second stage unit averages 37 percent solids with the acid in the pulp containing 3.5 percent phosphorus pentoxide and 2.5 percent sulphuric acid.

C. Filter

Slurry is carried to the filters by gravity in hard lead, Duro brick-lined launders fitted with hard lead launder covers. Filtration of the first stage slurry (45 percent gypsum, phosphoric and sulphuric acids and fluosilicates) is done in two 12 x 12 ft. Dorrco vacuum filters in parallel. The filter shells are of mild steel lined with 20-lb. hard lead both on barrel and ends. The panels, twenty in number, are divided from each other by hard lead bars placed longitudinally and burned to the sheet lead lining on the shell. Ports for removal of filtrate and air are cut in the bottom and at the center of each panel. Production acid (32 to 33 percent phosphorus pentoxide) drains out of the ports through 2-in. hard lead pipes running longitudinally on the outside of the shell around the discharge end of the filter and into the head valve. Drainage of acid from the head valve is through a rubber hose into a filtrate receiver, thence through barometric legs of hard lead pipe into pump sumps situated below the filter. The filter barrels are separated by longitudinal lead bars bonded through the sheet lead lining and steel filter shell.

Second stage filtration is accomplished in two similarly constructed 12 x 12-ft. Dorrco vacuum filters in parallel while third stage filtration is done in three 10 x 8-ft. Dorrco vacuum filters, also of similar construction.

D. Acid Pumps, Piping and Storage Tanks

Acid flows from the barometric legs of the filters into hard lead seal boxes and is pumped to wood stave lead-lined storage tanks by centrifugal pumps constructed of AISI type 316 stainless steel. All acid lines are of hard lead (5 to 6 percent antimony) flanged every 10 ft. Discharge lines from the AISI type 316 stainless steel pumps handling first stage slurry consist of 6-in. diameter hard lead pipe flanged every 10 ft, and lined throughout with medium hard rubber lining, a rather unique combination employed to reduce erosion from the slurry. All wooden storage tanks are lined with hard lead sheet.

E. Other Equipment

Phosphoric acid (20 percent P_2O_5) is measured by a Howard bucket-type feeder which consists of a hard lead lined steel tank containing a cast hard lead trunnion and cast hard lead buckets. This acid and 94 percent sulphuric acid flow to a hard lead lined fluorine stripper where air is blown into the mixture to evolve fluorine gas which is then exhausted to a recovery unit.

Production phosphoric acid (32 to 33 percent P_2O_5) is evaporated to a concentration of 36 percent P_2O_5 for feed to the ammonium phosphate fertilizer section of the plant. Swenson Evaporators of the low steam pressure horizontal tube type are used. These are constructed of cast hard lead sections bolted together and equipped with 196 Karbate (graphite bonded by plastic) steam tubes. Evaporators are not shown on the flow diagram.

5. CORROSIVES HANDLED

Hard lead (5 to 6 percent antimony) successfully handles the following corrosives encountered at various stages in the manufacture of phosphoric acid by the Dorrco Process.

a. Phosphoric acid - containing up to 36 percent P_2O_5 which roughly corresponds to a 50 percent concentration of phosphoric acid (H_3PO_4). (Lead may be used with all concentration of H_3PO_4 up to 80 percent below 200° C (392° F).) A typical analysis of production phosphoric acid:

P_2O_5	33.0 percent
Al_2O_3 + Fe	2.0 percent
Fluorine	2.0 percent
H_2SO_4	3.3 percent
H_2O	balance

b. Mixed acids - corrosion rate data for mixed acids are given in the table under section 6. The mixed acids in most cases consisted of a slurry containing an average of 38 percent solids by weight, largely calcium sulphate (gypsum) crystals. The slurry also contains both dissolved and undissolved fluosilicates.

6. PERFORMANCE

Through the courtesy of The Consolidated Mining & Smelting Company of Canada, Ltd., we are able to include a specially prepared report of comparative data on the corrosion resistance of lead and other materials in their phosphate plant operations. The following corrosion rates were determined by exposing corrosion spools in acid section solutions.

Corrosion Rate Data

	Conditions of Exposure				Corrosion Rate, in. Per Year				
Section	P_2O_5	H_2SO_4	Temp. °C	Time, Days	Hard Lead	Soft Lead	Stainless Steel 347	316	318
A	33%	2-3%	75°	33	Wt. Gain	Wt. Gain	.0004	.0006	.0004
B	20%	2-3%	60°	33	Wt. Gain	Wt. Gain	.0001	.0001	.0001
C	12-15%	2-3%	60°	32	Wt. Gain	Wt. Gain	.0001	.0001	.0001
D	3-10%	1½-2½%	60°	30	Wt. Gain	Wt. Gain	Wt. Gain	Wt. Gain	Wt. Gain
E	2-8%	½-1½%	65°	30	Wt. Gain	Wt. Gain	.0001	.0001	.0001

A) Production Acid
B) First Filtrate
C) Second Filtrate
D) Third Filtrate
E) Fourth Filtrate

In general the corrosion resistance of lead is excellent in solutions where sulphuric acid and phosphoric acid are present in sufficient quantities to form a portective film of lead sulphate and phosphate; the presence of sulphuric acid being probably more critical than that of phosphoric acid. Although all three types of stainless steel appear about equal to each other in the short term tests recorded above, experience has shown that AISI type 316 is to be preferred to AISI type 347 for general corrosion resistance and that AISI type 318 should be used whenever welding must be carried out in the field.

Experience has shown that acid proof brick laid directly on mild steel is not satisfactory since leaks invariably develop in the brick work and result in corrosion of the steel. The problem was solved by using an impervious lining of lead between the brick and steel.

Repair work on lead is easily accomplished in the field, but is usually necessary only in those locations where temperature is high and creep becomes a factor, such as in the first stage filters.

7. CONCLUSION

Production of phosphoric acid and phosphate fertilisers by The Consolidated Mining & Smelting Company of Canada, Ltd., Trail, B. C., commenced in 1931. The impetus to this development was given in the late 1920's by the need to recover sulphur dioxide, a by-product of the roasting and smelting operations of lead and zinc. To avoid possible damage to agricultural areas adjacent to the international boundary, the decision was made to build extensive contact sulphuric acid plants and sulphur recovery units capable of absorbing and fixing the sulphur dioxide gases. At the same time plants capable of utilising the sulphuric acid for the production of fertilisers were constructed.

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"Chemical Engineering" magazine reports that P_2O_5 consumption has increased steadily from about 1/2 million tons in 1933 to more than 2.1 million tons in 1949 and the capacity of plants making high concentration superphosphate fertilizer is continuing to grow significantly.

In the equipment in these installations used for handling either sulphuric acid, sulphur dioxide or phosphoric acid lead was chosen on a competitive basis as a practical material for protection against corrosive attack. Its use in the superphosphate fertilizer industry of which phosphoric acid manufacture is an integral part will undoubtedly continue to parallel the steady increase in demand for fertilizers.

8. REFERENCES

Additional details of the production of phosphoric acid are described in a paper by James Atwell entitled "Phosphate Processes at Trail, B C." in the July, 1949, issue of "Industrial and Engineering Chemistry."

The corrosion rate data given above is based on a private communication with The Research and Development Division of The Consolidated Mining and Smelting Company of Canada, Ltd. Construction details were obtained through the cooperation of the above company and The Dorr Company, Stamford, Conn.

The reaction of lead with phosphoric acid is described in Chemical Bulletin No. 5, a reprint from "Chemical Engineering."

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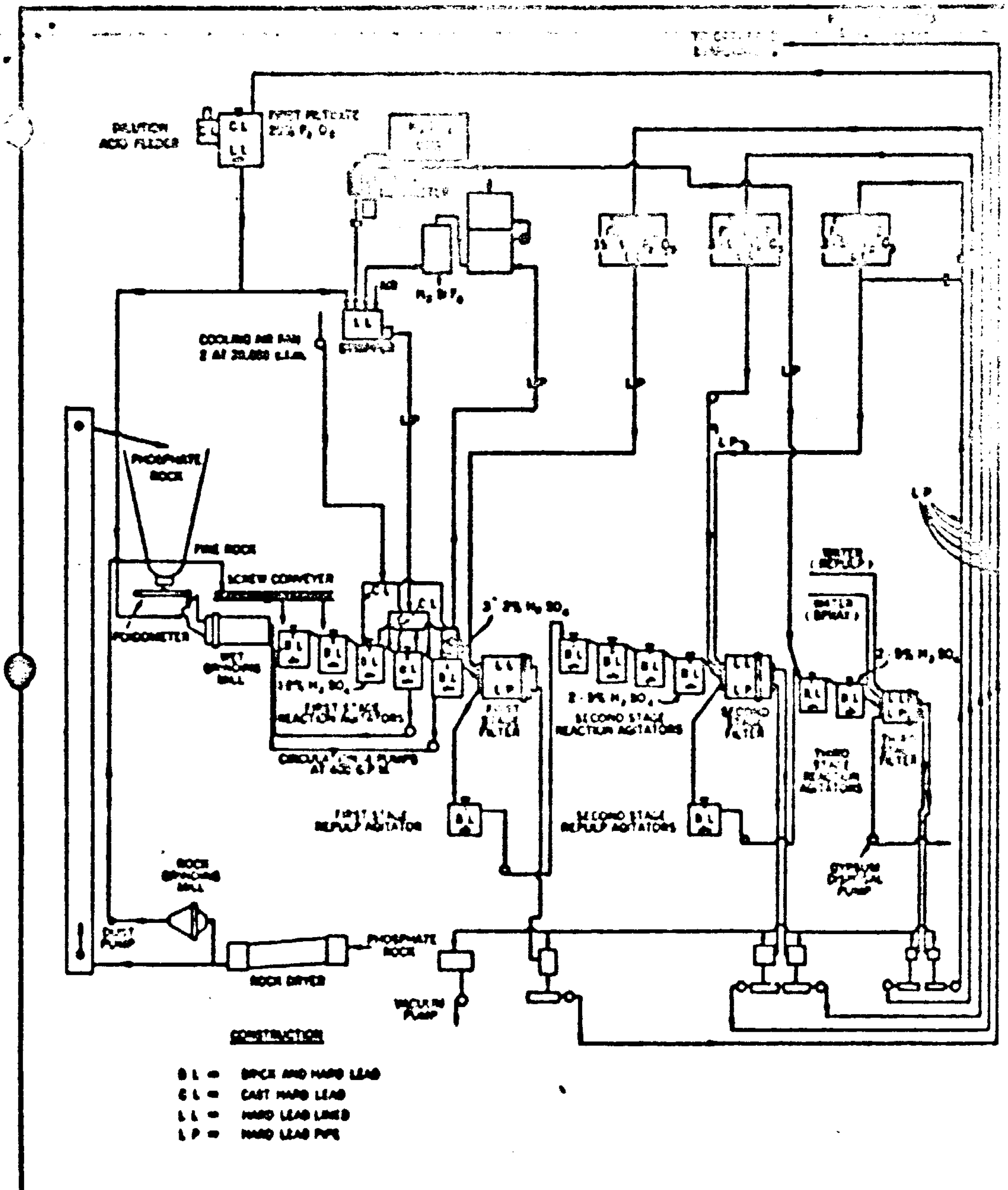

PHOSPHORIC ACID FLOW SHEET (DORR PROCESS)	LEAD INDUSTRIES ASSOCIATION	THE CONSOLIDATED MINING AND SMELTING CO. OF CANADA LTD.
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