TABLE VI—ANALYSIS OF SALT PRODUCED AFTER TREATMENT OF BRINE WITH SODIUM SULFATE

		Per cent Moisture	Per cent Insoluble	PERCENTAGES ON MOISTURE-FREE BASIS						BaCl ₂	SrCl ₂
				NaCl	MgCl ₂	CaCl ₂	CaSO ₄	BaSO ₄			
No. 2 Salt, the first produced after treatment.	10/9/15.....	10.06(a)	0.035	95.62	1.24	3.00	0.09	0.02	0.00		
No. 2 Salt, the first produced after treatment.	Sept., 1915.....	8.425(a)	0.038	95.44	1.30	3.01	0.18	0.03	0.00		
No. 2 Salt, 12 days after beginning treatment.	10/16/15.....	15.52	0.008	92.68	2.13	5.16	0.09	0.03	0.00		
No. 2 Salt, 19 days after beginning treatment.	10/23/15.....	13.12	0.018	93.84	1.81	4.38	0.11	0.01	0.00		
No. 2 Salt, 27 days after beginning treatment.	10/31/15.....	16.00	0.008	91.98	2.32	5.61	0.10	0.02	0.00		
No. 2 Salt, representative sample of above taken from warehouse.	11/1/15.....	5.91	0.023	97.22	0.80	1.97	0.08	0.04	0.00		
No. 1 Salt, after treatment.	9/19/15.....	5.247(a)	0.013	97.38	0.78	1.78	0.03	0.02	0.00		
No. 1 Salt, after treatment; collected in open market.	10/22/15.....	7.20	0.010	97.94	0.61	1.42	0.02	0.02	0.00		
Mixed Salt, No. 1 and No. 2 as delivered to warehouse.	Jan., 1916.....	10.22	0.010	96.54	1.00	2.39	0.01	0.01	0.00		
Mixed Salt, No. 1 and No. 2 after seasoning in warehouse.	2/16/16.....	3.73	0.010	97.58	0.72	1.68	0.00	0.02	0.00	0.05	
Mixed Salt, No. 1 and No. 2, from warehouse.	9/6/16.....	6.89	0.010	97.56	0.70	1.72	0.00	0.01	0.00		
No. 2 Salt, after treatment with equiv. Na ₂ SO ₄ .	Jan., 1916.....	14.01	0.037	93.80	1.80	4.30	0.00	0.04	0.01		
No. 2 Salt after treatment with equiv. Na ₂ SO ₄ . 1 mo. later.	2/16/16.....	10.55	0.035	90.30	2.83	6.70	0.00	0.02	0.04	0.14	
No. 2 Salt from grainer, after treatment with equiv. Na ₂ SO ₄ . 9 mos. later.	9/6/16.....	16.15	0.010	95.06	1.43	3.48	0.00	0.02	0.00		
ANALYSIS OF SALT BEFORE TREATMENT OF BRINE WITH Na ₂ SO ₄											
No. 1 Salt. From market. (11232-K).....	2.26		99.31	0.24	0.56			0.01			
No. 1 Salt. From warehouse (16097).....	5.97		98.24	0.51	1.22			0.03			
No. 1 Salt. From No. 3 grainer (16098).....	9.76		96.68	0.98	2.19			0.06	0.09		
No. 1 Salt. From warehouse (W. L. A).....	8.55		97.42	0.86	2.02			0.05			
No. 1 Salt. From warehouse (21416).....	8.33		97.42	0.76	1.85			0.02			
No. 2 Salt. From warehouse (21417).....	11.32		92.65	1.96	4.22			0.95	0.11		
No. 2 Salt. From warehouse (W. L. B).....	12.55		90.51	2.60	5.54			1.15	0.16		
No. 2 Salt. From warehouse (16099).....	7.35		95.04	1.10	2.58			1.18	0.09		
No. 2 Salt. Sludge salt from conc. bittern tank (16100).....	5.49		70.23	7.12	16.48			5.47	0.69		

(a) Moisture by difference.

market food salt which contains an appreciable quantity of barium. The highest content of barium found in the No. 2 salt has been 0.06 per cent, expressed as mixed barium sulfate and chloride. A sample, representing the mixed No. 1 and No. 2 salts, obtained from the works in February, showed 0.02 per cent barium sulfate. Since the installation of the process, the estimated production of salt by the works has been about 100,000 bbls. or approximately 14,000 tons.

The cost of treatment is low. Based upon the maximum capacity of the plant, 400 bbls. of salt per day, the actual cost of treatment, not including cost of original installation of tanks and equipment, and using an amount of sodium sulfate equivalent to the barium present, is approximately 0.5 cent per barrel, based on salt cake at \$12 per ton delivered at the plant. The cost of equipment, tanks, pumps, blower, pipe lines, etc., could not be definitely determined, since part of the equipment, for instance the compressed air system, had been installed previously for other purposes. A careful estimate places the cost of equipment and installation at about \$2,000. This is somewhat higher than a similar installation would cost at other plants, since the installation described necessitated an unusually high cost for foundation and emplacement of the storage tanks, due to the location of the plant on a very steep hillside. The interest on this investment and the depreciation of the equipment plus the labor cost, which it has been difficult to estimate, will not, it is believed, make the total cost of treatment over 1 cent per bbl., which is more than compensated for by the increased value of the product.

SUMMARY

The results may be summarized as follows:

I—The process enables the salt manufacturer to eliminate from the total product of the plant all but insignificant traces of an impurity which has been a constant source of concern.

II—The difference in the price of the heretofore off-grade salt, but which now forms a part of the first-grade salt, will more than offset the entire cost of the treatment.

III—The installation of the necessary equipment is a comparatively simple matter and does not necessitate any material change in the equipment at present employed in salt works.

IV—The application of the method eliminates the production of an off-grade salt and therefore removes from the market a potentially dangerous food product.

V—There is produced about 400 lbs. per day of barium sulfate as a by-product, for which it is expected to find a satisfactory market, although this has not yet been definitely determined.

BUREAU OF CHEMISTRY, WASHINGTON

THE USE OF THE COTTRELL PRECIPITATOR IN RECOVERING THE PHOSPHORIC ACID EVOLVED IN THE VOLATILIZATION METHOD OF TREATING PHOSPHATE ROCK

By W. H. ROSS, J. N. CAROTHERS AND A. R. MERZ

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The basis of nearly all mixed fertilizers is phosphoric acid in so-called available form as indicated by its solubility in water or in solutions of certain organic compounds. In this country phosphate rock constitutes by far the principal source of the phosphoric acid used in the manufacture of fertilizers. Other sources of relatively much less importance are bones, basic slag and certain organic wastes, such as fish scrap. The relative amounts of these different materials which enter into the fertilizer trade are governed by their supply rather than any difference in the fertilizing value of the materials. At present only one firm in this country is producing basic slag of sufficiently high grade to be used as a fertilizer. The supply of bones and fish scrap is also entirely inadequate to meet the present demands of the fertilizer trade. In the form of rock phosphate, however, phosphorus occurs in this country in such immense deposits that this source will undoubtedly continue to supply for an indefinite period the phosphoric acid used in the manufacture of commercial fertilizers.

The treatment to which phosphate rock is subjected in the manufacture of commercial fertilizers is still almost entirely limited to digestion with sulfuric acid

DIAGRAM OF PLANT USING THE COTTRELL PRECIPITATOR FOR THE RECOVERY OF VOLATILIZED PHOSPHORIC ACID

for the preparation of so-called superphosphate or acid phosphate. This process is a comparatively simple one and where cheap sulfuric acid is available or can be produced cheaply in districts where fertilizers are used in largest quantities, this method of making available the phosphoric acid in phosphate rock can be operated at a comparatively low cost.

There are many disadvantages, however, in making phosphoric acid water-soluble in the form of superphosphate:

1—Such a product is not suitable for mixing with considerable quantities of certain other fertilizers, such as lime, calcium cyanamid and sodium nitrate. Lime compounds have the property of reverting the acid phosphate back again into the insoluble form. Sodium nitrate does not have this effect on superphosphate but the acid properties of the latter, particularly if an excess of sulfuric acid is present, have a tendency to set free nitric acid from the nitrate with which it is mixed.

2—When continuously applied to certain soils deficient in lime the acid properties of superphosphate may tend to counteract in a measure the beneficial effects which the phosphate present might otherwise produce.

3—In the manufacture of superphosphate, ordinary chamber acid (50° Bé.) and ground phosphate rock are thoroughly mixed in equal proportions by weight and the mass allowed to cool for 24 to 36 hrs. The percentage of phosphoric acid in the final product will thus be only one-half as great as in the original

phosphate rock. It thus happens that the richest superphosphate that can be made by a single acid treatment of the highest grade phosphate mined in the United States contains only about 18 per cent of phosphoric anhydride. The remaining 82 per cent consists of gypsum, water of combination and the impurities occurring originally in the phosphate rock. Phosphoric acid being worth as a fertilizer only about 50 cents a unit wholesale, it follows that material of the nature of superphosphate will not admit of being shipped to places remote from where it is manufactured. For this reason, since the present market for phosphate fertilizers is to be found almost entirely in the eastern states, the superphosphate method is not considered to be applicable to the utilization of the extensive phosphate deposits occurring in the states of Utah, Idaho, Wyoming and Montana.

These disadvantages in the manufacture of superphosphate were early recognized and a great many processes have been proposed and patented with a view to producing soluble phosphates at a cheaper rate or in a more satisfactory way than are obtained with the superphosphate method. A compilation of these various processes has recently been made by Waggon and Fry¹ of this Bureau, who also give in brief abstract the processes employed, the treatment proposed and the new features claimed by the inventors. Those processes, which have to do with the treatment of phosphate rock, are classified by them as follows: (1) acid treatment which includes the man-

¹ U. S. Department of Agriculture, *Bull.* 312.

ufacture of superphosphate and phosphoric acid; (2) combined heating and acid treatment; (3) double decomposition by means of a silicate or an alkali; (4) processes used in connection with the steel industry; (5) processes in which the phosphorus or phosphoric acid is volatilized; (6) treatment dealing with the production of two or more fertilizer elements; (7) electrolysis; (8) enrichment or concentration of phosphates; (9) processes and apparatus for the mechanical treatment of phosphates; (10) miscellaneous processes.

As Waggaman and Fry have pointed out, the claims made for some of these processes are not justified while many other processes are entirely impractical from a commercial standpoint.

The processes which have attracted most interest during recent years, and which give most promise of replacing, in part at least, the sulfuric acid method, belong to Group (5) and have to do with the volatilization of the phosphorus from phosphate rock. All are based on the method long in use for the manufacture of elementary phosphorus and consist in igniting phosphate rock at a high temperature with or without one or more reagents such as coke and silica. The main advantages in this procedure lie in the fact that from rather impure raw materials there may be obtained comparatively pure phosphoric acid of high concentration which may readily be adapted to the preparation of fertilizers containing two or more fertilizing elements in concentrated form. Such a fertilizer would admit of shipment to places remote from where it is manufactured. The chief disadvantage of the superphosphate method in the utilization of the western phosphate is thus overcome by the volatilization method. As this method, moreover, is particularly adapted to the use of hydro-electric power it is probable that phosphoric acid prepared by volatilization will in the future compete as a fertilizer with that prepared in the form of superphosphate.

The processes of Wing,¹ Ruymbeke,² Landis,³ Washburn,⁴ Haff,⁵ and Hechenbleikner,⁶ all call for the ignition of phosphate rock with coke and silica in an electric or blast furnace at such temperature that the phosphate radical is replaced by the silica and in the presence of the reducing atmosphere caused by the coke, the phosphorus is first volatilized in the elemental form to be at once changed into phosphoric acid by oxidation with air and absorption in water.

In the processes proposed by van Denbergh,⁷ De Chalmot,⁸ Levi,⁹ Haff,¹⁰ Haff and Willson,¹¹ and Willson and Haff,¹² the use of coke is omitted and the phosphate rock is simply ignited with sand or some other siliceous material as feldspar.

¹ United States Patent No. 452,821.

² United States Patent No. 540,124.

³ United States Patent No. 859,086.

⁴ United States Patents Nos. 1,044,957, 1,047,864 and 1,100,639.

⁵ United States Patent No. 1,084,856.

⁶ United States Patent No. 1,112,211.

⁷ United States Patent No. 669,271.

⁸ United States Patent No. 689,286.

⁹ United States Patent No. 984,769.

¹⁰ United States Patent No. 1,018,186.

¹¹ United States Patent No. 1,076,499.

¹² United States Patent No. 1,103,910.

In Morehead¹ and Duncan's² processes, on the other hand, for producing elementary phosphorus the siliceous material is omitted and the phosphate rock ignited with coke or other reducing material.

According to Maywald,³ phosphorus pentoxide may be volatilized from phosphate rock by simply passing an electric current through the latter in a furnace to which air is admitted.

The processes proposed by Machalske⁴ differ from any of the others in that the ground rock is ignited with a mixture of sodium chloride and coke. The phosphorus chloride formed is led off and treated with water to form phosphoric acid and hydrochloric acid. It is suggested that the carbide remaining in the furnace may be used in the fixation of atmospheric nitrogen.

Of these different processes for treating phosphate rock those which apparently offer most promise involve the use of both silica and coke. In experiments made in this laboratory it was found that when the rock was ignited with these two reagents, the phosphorus was driven off much more readily and completely and at a lower temperature than when the ignition was made with either of them alone.

The feasibility of the process as a method of extracting phosphoric acid from phosphate rock has been demonstrated by the large scale operations which have been carried on in a commercial way at Mt. Holly, N. C., under the rights of the Hechenbleikner⁵ patents.

The furnace used in this plant has a capacity of 5,000 kw. and is operated by a 3-phase alternating current at 250-300 volts. The charge consists of a mixture of phosphate rock, sand and coke in such proportions that the quantities of silica and carbon in the charge are about 20 per cent in excess of that required by the equation:

This charge is fed into the furnace through openings around the electrodes. In this way the double purpose is served of permitting the electrodes to be adjusted without allowing the fumes of phosphorus to escape, and the cool charge likewise forms a protection against too rapid oxidation of the electrodes. As the phosphorus is driven off it is first oxidized with air in an oxidizing tower and then passed through a series of scrubbing towers where absorption of the oxides takes place. By circulating the solution through the towers a solution may finally be obtained containing as high as 50 per cent of phosphoric anhydride. With the solution thus recovered there may be prepared ammonium phosphate by neutralizing with ammonia; or by treating a fresh lot of phosphate rock with a quantity of acid equivalent to the phosphoric acid in the quantity of rock taken, there may be prepared double superphosphate which contains upwards of three times the percentage of phosphoric

¹ United States Patents Nos. 862,092 and 862,093.

² United States Patent No. 733,316.

³ United States Patent No. 902,157.

⁴ United States Patents Nos. 709,438, 789,439 and 789,440.

⁵ United States Patents Nos. 1,112,211, 1,167,755 and 1,173,960.

anhydride that is contained in superphosphate made in the ordinary way from the same phosphate rock.

A number of disadvantages, however, attend the scrubbing tower method of recovering the oxides of phosphorus when volatilized in the way described:

(1) Notwithstanding the extreme hygroscopic nature of phosphorus pentoxide it is nevertheless not readily absorbed by water when volatilized from phosphate rock and complete absorption can be effected only by a more or less extended series of towers provided with a system of baffle plates over which water is made to circulate.

(2) The acid has an injurious effect on all metal parts required in the pumping system necessary for maintaining a circulation of the solution through the towers.

(3) The hydrofluoric acid evolved in the process from the fluorine occurring in the phosphate rock also acts injuriously in the case of any extensive absorbing system, and it is considered by those engaged in the practical operation of this process that the hydrofluoric acid has a retarding effect on the absorption of phosphorus pentoxide as evidenced by the observation that the absorption of the pentoxide from phosphate rock free from fluorine takes place more readily than from rock which contains fluorine.

(4) By use of scrubbing towers it has been found impractical to obtain a solution containing more than 50 per cent phosphoric anhydride. When such a solution is neutralized with ammonia gas to make mono-ammonium phosphate the product obtained will contain about 25 per cent of water and will consequently have to be dried before being placed on the market. Drying is also necessary in the manufacture of double superphosphate, which adds considerably to the cost of manufacture.

It has occurred to the authors that by the use of the Cottrell precipitator in place of the scrubbing tower system now used for collecting the fumes evolved from the furnace, most if not all of the disadvantages cited might be avoided.

The results which have now been obtained with the precipitator in experiments undertaken on a fairly large scale have justified expectations, and it has been found that the chemical and physical properties of phosphorus pentoxide are such that the Cottrell precipitator is particularly adapted to its precipitation in the form of phosphoric acid.

The furnace used in these experiments consisted of an iron cylinder lined on the inside with fire brick, and provided with an opening near the bottom for the removal of the slag. The 3-phase alternating current used was stepped down from 220 volts by two single-phase 75 K. V. A. transformers. Each transformer was provided with a split primary and by joining in different combinations in series and in parallel the coils in the secondary different voltages could be obtained, varying from 40 to 100 in steps of 20, and also halves of these voltages.

In the preliminary experiments there was used an absorbing tower 18 ft. high and 4 ft. square cross section with an effective absorption surface of about

3,000 sq. ft. These experiments demonstrated the difficulty of recovering all of the phosphoric acid by this means.

When the Cottrell precipitator was installed the gases in the first series of experiments were still allowed to pass through the tower, but with no water present. This then simply served as a baffle tower and as a means of cooling the gases, thereby permitting experiments to be made on the precipitation of the phosphoric acid at temperatures but little above the ordinary temperature.

The power used in the precipitator was provided by a 110 volt, 60 cycle, alternating current motor-generator set, and was stepped up by an 8 K. V. A. transformer capable of yielding voltages of 10,000, 20,000 and 40,000 volts. In these experiments the highest voltage only was used. From the transformer the current was changed to intermittent d. c. by a small mechanical rectifier attached to the shaft of the generator and so adjusted as to operate in synchronism with it. The positive lead from the d. c. side of the rectifier was earthed while the other terminal was connected to the wires suspended in multiple, one in each of the pipes used in the precipitator. Each pipe was then earthed. In the accompanying diagrammatic sketch is represented the equipment used in these experiments.¹

In the preliminary experiments made with the precipitator, sheet iron pipes were used, 6 in. in diameter and 10 ft. high. The precipitated acid, however, had such a corrosive action on the pipes that they had to be abandoned. Pipes were then constructed from ordinary 6-in. glazed terra cotta tile, 5 sections being taken for each pipe. The precipitated acid gave to the inside of the pipes an effective conductive surface and in grounding the pipes it was found sufficient simply to bring the ground wire to the inside surface of each pipe at one point. Arranged in this way the terra cotta pipes could be used just as efficiently in the precipitation of the acid as metal pipes and they had the very important advantage of being unaffected by phosphoric acid. Wires of monel metal were found to be least acted upon when suspended in the pipes but nichrome wire also served quite well. Weights were suspended at the ends of the wires and individual oscillations were prevented by a wire connecting all the weights.

The fumes evolved from the charge in the furnace were drawn off by the suction of an exhaust fan, constructed of antimonial metal, through which the gases passed before entering the precipitator. The inside of the fan was coated with Bakelite enamel to prevent contamination of the acid by the metal of the fan. Entrance of air into the furnace was allowed to take place around one or more of the electrodes, and the charge fed in around one or more of the others. In this way oxidation of the evolved phosphorus was effected in the furnace as it issued above the charge.

The capacity of the fan used in drawing off the fumes from the furnace was 450 cu. ft. per minute.

¹ An expression of appreciation is due H. Bryan of this laboratory who had charge of installing a part of this equipment.

As shown later, this flow of air was much in excess of that necessary to oxidize the phosphorus evolved from the furnace. Using a fan of this capacity it was found necessary to use 6 pipes to bring about complete precipitation of the fumes. By cutting down the volume of air treated the number of pipes necessary might be reduced in proportion. Moreover, with a higher potential than was available, pipes of even double the diameter might be used. In a plant of commercial size, therefore, the increase in the capacity of the furnace over that which we used should call for a much less proportionate increase in the number of pipes.

Since the phosphorus passes off from the furnace for the most part in the form of phosphorus pentoxide it might be expected at first thought that it would be collected as such in the precipitator. A simple calculation will show, however, that this is not practical for there will always be enough moisture in the charge used and in the air required to oxidize the phosphorus evolved to convert the phosphorus pentoxide either in whole or in part into phosphoric acid.

Thus in air saturated at, say 20° , and of sufficient volume to supply the gram molecules of oxygen called for in the equations, $\text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 + 5\text{C} = 3\text{CaSiO}_3 + 5\text{CO} + 2\text{P}$; $\text{CO} + \text{O} = \text{CO}_2$; and $2\text{P} + 5\text{O} = \text{P}_2\text{O}_5$, there are 9.9 grams of water, sufficient to convert 18 per cent of the pentoxide into orthophosphoric acid. If it be assumed, moreover, that the phosphoric acid in the phosphate rock amounts on an average to 19 per cent of the charge used, and that the moisture in the latter amounts to, say, 5 per cent, then this source of moisture will be equivalent to a further 69 per cent of the phosphorus pentoxide.

By increasing the quantity of water vapor passing into the precipitator, acid of any dilution may be obtained; conversely, if the air is dried before entering the furnace and likewise the charge used, the evolved phosphorus pentoxide should be precipitated in the solid state, but from a commercial point of view there would be little or no advantage in collecting the phosphorus pentoxide as such on account of the extremely hygroscopic nature of this material.

This hygroscopic nature of phosphorus pentoxide makes it particularly adapted to precipitation with the Cottrell precipitator. If it precipitated in a flocculent state as it occurs in the anhydrous form, or in a pasty condition too thick to run down the sides of the pipes its recovery with the precipitator would be a matter of difficulty. In our experiments, however, it was found that there was always an excess of moisture in the air drawn through the furnace and in the charge used above that necessary completely to convert the phosphorus pentoxide into phosphoric acid. This was then precipitated in the form of a solution which ran down the sides of the pipes and was collected in a continuous stream from the delivery tube leading from the stoneware receiver, which also served as a baffle in the box which supports the precipitating pipes as shown in the sketch.

When the fumes were passed through the tower and precipitation thus made at a temperature but

little above normal, the concentration of the acid first collected was in the neighborhood of 60 per cent phosphoric acid. The moisture content of the charge used amounted to only about 1 per cent. From the calculation already given it must follow therefore that the rate of air which was passed through the furnace to carry off the fumes must have been much in excess of that necessary to oxidize the phosphorus evolved. On cutting down the flow of air somewhat the concentration of the acid was increased to about 80 per cent, and it is quite evident that with the humidity of the air remaining the same a still more concentrated acid might be obtained by still further limiting the flow of air through the furnace. It was thought, however, that without changing the rate of flow of the air through the furnace a more concentrated acid might also be obtained by increasing the temperature at which the precipitation was made.

In carrying out experiments on the precipitation of the acid at higher temperature, the baffle tower was cut out and the fumes passed directly into the precipitator through the terra cotta by-pass as shown in the sketch. Under these conditions the fumes from the furnace entering the precipitator reached in the course of two or three hours a temperature of about 175° and remained fairly constant at this temperature for several hours longer. In passing through the pipes the temperature of the gas fell to about 100° . As shown in Table I, the concentration of the acid collected in this way, with either a maximum or minimum flow of air passing through the furnace, was considerably in excess of that collected in a corresponding way at a lower temperature.

TABLE I—VARIATION IN CONCENTRATION OF ACID WITH THE TEMPERATURE OF PRECIPITATION AND WITH THE FLOW OF AIR THROUGH THE FURNACE

Temperature of Precipitation	Flow of Air through Furnace	Sp. gr. 25°/25° of Acid Collected	Concentration of Acid, Per cent H_3PO_4
About 30°C	Maximum	1.448	63.07
About 30°	Minimum	1.630	80.23
About 100°	Maximum	1.766	90.82
About 100°	Minimum	1.800	95.23

In Table II are given analyses of two samples of phosphoric acid collected on different dates and which are thought to represent extremes as regards impurity in the samples of acid so far collected.

TABLE II—ANALYSES REPRESENTING EXTREMES AS REGARDS IMPURITY IN THE PHOSPHORIC ACID COLLECTED IN THE COTTRELL PRECIPITATOR

	A	B		A	B
H_3PO_4	63.68	63.07	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$..	0.06	Trace
H_2SO_4	0.21	0.04	Arsenic.....	Trace	Trace
HF	0.49	Trace	Heavy metals..	None	None
HCl	0.04	None	Residue on igniting to redness.....	0.85	0.11
SiO_2	0.26	0.03			
CaO	0.03	None			

The rock used in these experiments consisted of Florida land-pebble phosphate and was used without grinding. The phosphorus present amounted to 32.14 per cent expressed as P_2O_5 and the fluorine to 2.33 per cent. If all the fluorine as well as all the phosphorus were volatilized and precipitated, then the hydrofluoric acid in a phosphoric acid solution of the concentration of, say, Solution A, Table II, should amount to 3.52 per cent. Likewise, since the coke used contained 2.56 per cent of sulfur expressed as SO_3 , the percentage of sulfuric acid in the

same phosphoric acid solution, if all were volatilized and precipitated, would amount to 0.75 per cent. Since the amounts of hydrofluoric and sulfuric acids found even in Solution A form only a comparatively small part of that which would be present in the phosphoric acid if all were volatilized and precipitated, it is evident that under the conditions of the precipitation the greater part of the hydrofluoric and sulfuric acids pass through the apparatus in the form of gas and are therefore not acted upon by the precipitator.

The acid collected when the fumes were passed through the baffle tower contained in suspension a slight amount of insoluble material consisting mostly of volatilized silica, but when this was removed by filtering, or by decantation on settling, the acid obtained was then perfectly transparent. When the baffle tower was cut out, the acid collected naturally contained a larger amount of suspended matter with a consequent small increase of bases in solution and was somewhat colored, due, no doubt, to carbonaceous matter carried over with the current of air.

By operating the furnace continuously and by reducing the amount of heat radiated, it should be possible to pass the fumes from the furnace through an efficient baffle tower and yet make the precipitation at temperatures above 100°. Judging from the results already obtained, the acid collected under these conditions should be of sufficient purity for use in those industries where a relatively pure acid is required. To prevent contamination of the acid in its preparation the precipitator must be made of stoneware or porcelain and all metal must be avoided in all parts of the equipment that come in contact with the fumes. In the manufacture of phosphoric acid for use in fertilizers these special precautions for collecting pure acid would of course be unnecessary.

SUMMARY

An investigation on a semi-commercial scale has been made of the use of the Cottrell precipitator in recovering the phosphoric acid evolved in the volatilization method of treating phosphate rock by ignition with coke and silica in an electric furnace. A current of air which was passed over the charge in the furnace served the double purpose of oxidizing the fumes of phosphorus to phosphorus pentoxide and of carrying the latter to the precipitator. In one series of experiments the fumes from the furnace before entering the precipitator were passed through a tower provided with baffle plates which had the effect of cooling down the gases to about ordinary temperature. In a second series of experiments the tower was cut out and the fumes passed almost directly into the precipitator at a temperature above 100°. In each case the phosphorus pentoxide, which takes up water from the current of air passing through the furnace and also from the moisture driven off from the charge, is precipitated in the form of a solution of phosphoric acid. When the precipitation is made at temperatures of about 100°, or above, the concentration of the acid is greater than that collected

at a lower temperature, but by reducing the flow of air through the furnace, acid of high concentration may also be obtained with low temperature precipitation.

The advantages of this method of collecting the phosphoric acid over the scrubbing tower method now in use are as follows:

1—The equipment required is simple in construction and automatic in operation.

2—The simplicity of the construction of the precipitating pipes decreases the difficulties arising from the corrosive action of the phosphoric and hydrofluoric acids evolved from the phosphate rock.

3—In this way there may be recovered phosphoric acid of a high degree of purity suited for direct use without further purification in those industries where a relatively pure acid is required.

4—A more concentrated acid can be obtained in this way than is possible to prepare directly by any other commercial process, and when this acid is used in the preparation of concentrated fertilizers, such as mono-ammonium phosphate, a dry product may be obtained directly without the necessity of evaporating solutions, or of drying the resultant product.

This is the first time that the Cottrell precipitator has been used for the precipitation of a product which has been purposely volatilized with a view to its recovery in this way.

BUREAU OF SOILS
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EMULSIONS AND SUSPENSIONS WITH MOLTEN METALS¹

By H. W. GILLET²

The object of this paper, which is written at Prof. Bancroft's request, is not to present any new information, but to suggest a line of thought.

In the refining of aluminum chips to ingot a loss of 30 per cent of the metallic content is common and a 15 per cent loss represents very good practice. In a study³ of these losses it was found that the cause for the high loss is not primarily the ease of oxidation of aluminum, but the failure of the globules to coalesce; that is, the loss is not due to oxidation in the furnace unless abnormally oxidizing conditions obtain there, and is not preventable by retorting, vacuum furnaces, electric furnaces, etc. Commercial aluminum chips from the machine shops of the automobile manufacturers contain about 20 or 30 per cent of the total weight that will pass a 20-mesh sieve and are about 0.005 in. thick. There is usually not less than 3 per cent and sometimes 15 per cent of cutting oil or compound and usually not less than 5 per cent and sometimes 15 per cent of very fine dirt, such as floor sweepings mixed with the chips.

If one tries to melt down aluminum chips in the way brass chips would be melted, the larger and thicker

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³ H. W. Gillett and G. M. James, "Melting Aluminum Chips," Bureau of Mines, Bull. 108 (1916).