Phosphoric Acid Manufacturing Through Hydrochloric Acid Route by Solvent Extraction

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Summary: The production of high grade phosphate fertilizers requires a good quality phosphoric acid since it is an important raw material for these industries. The present report describes an efficient and economical route for manufacturing phosphoric acid by treating rock phosphate with commercial hydrochloric acid followed by its separation from the crude mixture by solvent extraction using amyl alcohol as solvent. The acid, obtained by this method, is of high quality and could be upgraded up to density of 1.5 g/mL at 25 $^{\circ}$C.

Introduction

Phosphoric acid is an important chemical used mainly as an intermediate by fertilizer, soap, detergent, food, beverages, metal industries and in HPLC as part of mobile phase [1,2]. Phosphoric acid is manufactured in different parts of the world from rock phosphate (phosphorite) by acidulation with different mineral acids such as sulfuric, hydrochloric or nitric acid, *etc.*, or by burning of phosphorus produced through electro-thermal process [3]. Acidulation of rock phosphate with sulfuric acid is mostly preferred for the production of fertilizer grade phosphoric acid, and may be classified according to the hydrate form in which calcium sulphate crystallizes *viz* anhydrate ($CaSO_4$), hemihydrate ($CaSO_4.l/2H_2O$) and dihydrate ($CaSO_4.2H_2O$) *i.e.* mostly dihydrate and hemihydrate processes are important ones [4-6]. Another attractive route for production of good quality phosphoric acid starts from acidulation of rock phosphate with hydrochloric acid yielding a mixture of phosphoric acid and salts as impurities like $CaCl_2$, $FeCl_3$, $FeCl_2$, $AlCl_3$, $MgCl_2$ *etc*. The soluble nature of these salts make the separation of phosphoric acid by decanting or filtration quite difficult, but solvent extractions allow efficient separation [7]. We report herein an economical method using amyl alcohol for solvent extraction of phosphoric acid from hydrochloric acid-treated rock phosphate, which opens a new methodology for commercial production of highly pure phosphoric acid which is not restricted by numerous patent applications [3].

Experimental

Acidulation of Rock Phosphate by Hydrochloric Acid

Rock phosphate, when treated with hydrochloric acid, is decomposed to give mainly phosphoric acid and chlorides of calcium, iron, magnesium, aluminum as impurities. The acidulation reaction was carried out at 52 ± 1 $^{\circ}$C, using commercial hydrochloric acid (31%). After analysis of the mother liquor, the CaO/P_2O_5 ratio was optimized and analysis was done by standard fertilizer methods using a Shimadzu 1700 Pharma Specs UV spectrophotometer, and an atomic absorption Varian 1475 AD instrument.

Liquid-Liquid Contaction

Crude phosphoric acid was mixed with amyl alcohol at ratios varying from 1:1 to 1:3.5. Small amounts of acetaldehyde were also added to improve the extraction efficiency from 41 to 65%. Raffinate phase which is rich in impurities was recycled to fresh the extract phase to minimize phosphoric acid losses and extraction has been completed in three stages.

Stripping of Phosphoric Acid from the Extract Phase

To the extract phase, loaded with phosphoric acid, distilled water was added. There upon an organic phase containing the alcohol and an aqueous phase having the phosphoric acid separated sharp and quickly.

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Concentration of Product Acid

Phosphoric acid, thus obtained, was weak in strength having 4.80% P_2O_5 and was concentrated up to 50% P_2O_5 by estimating the level of impurities which are separated by post-precipitation.

Results and Discussions

The acid-rock ratio is very important for the efficiency of the acidulation process [8-13] and several experiments were conducted for evaluation of optimal acid-rock ratio conditions (Table-1). The results demonstrate that maximum P_2O_5 recovery is achieved from an acid-rock ratio of 1:1.2 w/v. The decomposition of phosphate rock with hydrochloric acid is an exothermic process, however, it was observed that temperature does not rise to the limit required for the maximum decomposition of rock therefore the mixture is heated to 52 ± 1 °C whereby the rock is completely acidulated. It was imperative to keep the reaction mixture undisturbed 52 ± 1 °C for a period of two to two and half hours for complete sedimentation. The phosphoric acid mixture, thus, obtained was analyzed and the composition was determined to be as follows: P_2O_5 (8.26%); CaO (13.80 %); Fe_2O_3 (1.03~1.16%); and Cl (19.7~20.1%).

Extraction conditions were optimized and maximum concentration of P_2O_5 was extracted when acid /alcohol ratio was kept at 1:2 and extraction efficiency reaches a maximum of 65% (Table-2). Decreases in extraction efficiencies may be due to an increase in dilution of the phosphoric acid mixture. The concentrations of P_2O_5 seem to play an important role on the selection as well as on the extraction efficiency of the solvent.

Stripper of phosphoric acid from the extract phase was carried out with distilled water an excellent solvent of the acid. Phase separation was quick and there was no turbidity at the junction of organic and aqueous phase. The acid produced was concentrated in an open pan evaporator up to a density of 1.5 g/mL at 25 °C. The impurities such as Fe_2O_3, Al_2O_3, MgO, CaO, *etc*, can be removed by partial stripping of the extract phase with small amount of water and was found experimentally good for the removal of cationic impurities in particular. The raffinate which is rich in impurities along with phosphoric acid is recycled to fresh extract phase which aids to further decrease the impurities to traces. Stripped acid is then passed through activated charcoal and fuller earth (activated clay) to remove organic traces. The comparative analytical data obtained for the crude and finally purified phosphoric acid clearly demonstrate that the impurities levels were eliminated to a greater extent (Table-3).

Recovery of Solvent

The solvent, separated after complete stripping of the acid contains 2-3% of water as amyl alcohol has less water miscibility as compared to other alcohols which are conventionally used for acid extraction. The alcohol can be recovered from the raffinate phase by vacuum distillation at 110 °C. The stripped acid also contains a small fraction of the solvent that could also be recovered by vacuum distillation at about 60 °C. The extraction efficiency of the recovered solvent was found to be same as that of the fresh solvent which makes this process economically feasible. The whole process is depicted in Figure-1.
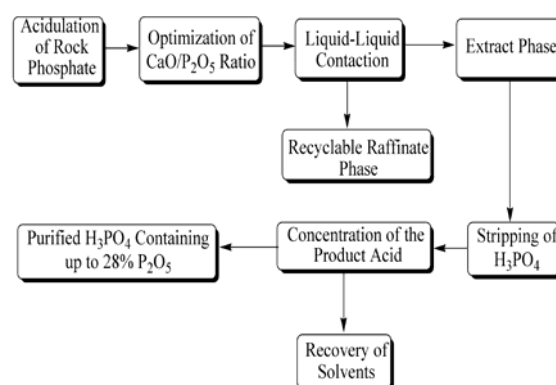

Fig. 1: Flow sheet diagram of the process.

Conclusion

It is obvious from the data that good quality phosphoric acid could be manufactured through the HCl route using low quality indigenous rock phosphate. The acid, manufactured through this process using amyl alcohol as solvent, is technically feasible. Extraction of phosphoric acid with amyl alcohol allows eliminating impurities up to a great extent and yields phosphoric acid of good quality which can easily be concentrated. Recovery of the amyl alcohol from different stages of the process is found to be convenient due to low water miscibility, and its re-extraction efficiency is comparable to that of fresh solvent. Moreover hydrochloric acid needed for the process is a cheap by-product of the soda ash industries and it is surplus in most of the countries and can effectively be utilized for the manufacturing of phosphoric acid a valuable industrial intermediate with multiple applications.

Table-1: Decomposition of Eastern Rock.

Acid/rock ratio	Percentage Decomposition in						
	2.5 Minutes	5 Minutes	10 Minutes	20 Minutes	40 Minutes	60 Minutes	90 Minutes
1:0.52	57.90	59.47	61.35	62.43	64.97	68.68	-
1:0.78	73.57	74.19	75.09	75.95	79.31	81.23	-
1:1.04	86.26	87.12	89.02	90.01	93.28	96.59	-
1:1.31	84.54	87.31	91.23	93.70	95.91	98.39	98.44
1:1.57	85.71	88.83	91.02	92.53	96.47	99.21	99.23
1:1.83	84.59	87.37	91.19	91.19	95.89	98.28	98.31

Table-2: Optimization of Extraction Conditions.

Acid/alcohol ratio	Organic Phase (g)	Raffinate (g)	P_2O_5 in Organic phase (%)	P_2O_5 in Raffinate phase (%)	P_2O_5 in Organic phase (g)	P_2O_5 in Raffinate phase (g)	Exraction Efficiency (%)
1:1.0	57.13	41.80	3.06	5.73	1.748	2.35	42
1:1.5	83.69	40.42	3.06	5.27	2.55	1.55	64
1:2.0	110.38	38.50	2.43	4.56	2.68	1.42	65
1:2.5	137.78	37.64	1.75	4.97	2.41	1.69	50
1:3.0	162.60	36.60	1.54	4.85	2.50	1.60	60
1:3.5	188.20	36.00	1.34	4.62	2.52	1.56	61

Table-3: Composition of Pure and Crude Phosphoric Acid.

	Crude Acid (%)	Concentrated Acid (purified) (%)
P_2O_5	8.20	28.000
CaO	12.65	0.018
Cl	15.78	0.0013
F	0.52	0.0015
Fe_2O_3	0.54	0.0004

Acknowledgements

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