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Novel Technique for Purification of Fertilizer Phosphoric acid with Simultaneous Uranium Extraction

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Abstract

A process codenamed PHOSPURIN is described for the purification of Fert Phosphoric acid with simultaneous extraction of Uranium compounds from acid. This includes maintaining the acid stream at different redox potentials for the necessary extraction of all the metals & rare earths using Solvent Extraction technique. Details are also provided on the extraction behavior of various cations and rare earths from fert acid media employing redeveloped Phosphate reagent (codenamed KROPHOS-18) in kerosene system.

The effects of various parameters, such as the concentration of acid, metal ion and extractant, nature of the diluents etc., on the extraction of various cations have been investigated. Based on the extraction data, most of the cations like Fe (II) & (III), Al, Mg, Ca, Mn, Na, K, heavy metals like Arsenic / Cadmium, rare earths including Uranium etc., are all being extracted with high to very high separation factors from all molar fertilizer phosphoric acids.

The practical utility of the extractant & the process has been demonstrated by tests on commercial fert phosphoric acid. It has been conclusively found that KROPHOS-18 has good properties, such as high distribution coefficient, good stability, acceptable kinetics, good phase separation etc.

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1. Introduction

1.1. General

Water Soluble fertilizers (WSF) are gaining popularity by the day for their high purity and water-solubility making them an ideal fertilizer for fertigation and for foliar application. Technically pure Phosphoric acid is a primary raw material for producing such WSF products as well as various other downstream technical grade phosphates. Purification of acid also eliminates the transfer of harmful metals like Arsenic, Cadmium & Uranium to downstream products & processes.

To meet the growing requirement of high purity phosphoric acid, solvent extraction technique and novel phosphorus based KROPHOS-18 extractant developed indigenously have been successfully tested.

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This author therefore has taken a lead & initiative on the development of this twin novel approach to establish both purification of Fert Phosphoric acid while also simultaneously recovering Uranium in a separate stream. The process has been codenamed PHOSPURIN.

With constant rise in demand of energy, it is apparent that the world cannot rely on hydroelectric, gas / oil, coal, wind and biomass only for energy. In comparison, Nuclear power provides the lowest cost, safest and cleanest source of energy.

Despite Fukushima's negative impacts, there are numerous reasons for the growth of global nuclear power, including a world hungry for all forms of energy and increased concerns over the greenhouse gas emissions. This has also once again revived the interest of fertilizer manufacturers worldwide to develop facilities for the extraction of uranium from fert acid.

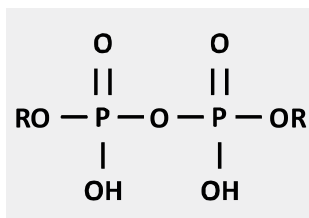
1.2. Background of Invention

Solvent Extraction is an attractive alternative for the recovery of metal ions from various solutions. In case of fert phosphoric acid, it is used to extract most of the polluting cations from the acid. Various Phosphorus extractants such as DEHPA7, 9, 15, TBP3, OPPA1, 12, DBBP18, APPA4, 10, TOPO7, 9, 15 etc., have been studied to purify green acid / extract Uranium since 1950's. Amongst these, currently TBP has been utilized commercially for acid purification. Though enormous information is available on metal extraction parameters with above reagents in other mineral acid systems, relatively less information exists on extraction characteristics of Pyro phosphoric acids on purification of phosphoric acid.

Alkyl Pyro Phosphoric acid came into prominence as extractant in the late fifties and the sixties for the extraction of uranium and other rare earths from fertilizer acid. During such U+ extraction, simultaneous acid purification was ignored, priority being Uranium. Though this process was used commercially in some plants for some period in Florida, USA, the operations were later discontinued due to the unstable nature of Pyro Phosphoric acid & low uranium price. During the last four decades, Alkyl Pyro Phosphoric acids have been avoided due to their unstable nature & availability of better reagents.

Section headings

Pyro Phosphoric acids are represented by the general formula –



Its distribution coefficient measures 30 – 40 for Uranium in fert phosphoric acid. A coefficient of this magnitude has a number of advantages, some of which include –

- Smaller amount of reagent required
- Fewer extraction stages
- Smaller equipment and thus CAPEX savings
- Extraction of metal in concentrated form
- Lower (OPEX) production cost etc

KROPHOS-18 has been stabilized by a unique method of synthesis by the author himself. The reagent which is well known to have one of the highest coefficients of extraction amongst all the current phosphate reagents can hold metal ions stoichiometrically equivalent of its molar concentration. KROPHOS-18 samples were used for the current tests.

1.3. Phos acid & Solvent Extraction

Phosphoric acid manufactured from elemental phosphorus route dominated the technical grade acid supply scenario in the early 1960's & 70's. There were no any such major commercial processes developed on industrial scale to purify fertilizer acid during that period. It was only the after the increase in the energy prices during 70's that the elemental

phosphorus route started getting uneconomical & experts around the globe started searching alternatives to this route. By the end of the 1970's & the beginning of the 80's several dominant players in phosphoric acid industry came out with SX technologies to purify acid, the only viable replacement available to elemental phosphorus route.

Varied reagents such as those of Amides, Ethers, Ketones, Secondary Amines with Aliphatic side chains, Quaternary Ammonium compounds, Sulphonic acids, Mixtures of Alcohols, high molecular weight Tri-alkyl tertiary amines & various kinds of Phosphate esters have been used to purify fert. acid. The 1980's saw the birth of certain other processes developed by several companies such as:

- Phospurex process by Luwa Ltd, used Iso-butanol to purify acid
- IPROCHIM (Romania) process too used Iso-butanol in their SX process
- Prayon process uses a mixture of Di Iso Propyl ether & TBP to purify the acid
- SX processes developed by USS Agri-Chemicals & Occidental Oil
- The Rhone-Poulenc Central liquor process used TBP to purify the acid
- The BESA-2 process by Bechtel used ketones to purify the acid
- Toyo Soda developed Two processes one involving HCL & other H₂SO₄
- Urea Phosphate/Methanol Ammonia technologies by TVA, Alabama USA
- Process developed by Albright & Wilson Ltd. using MIBK as the solvent
- Hoechst Ag of Germany also developed a solvent extraction purification Process
- Albright & Wilson Ltd used another process of crystallization to purify acid
- Ion Exchange resins process by W. R. Grace & Co. to purify the acid
- Uranium Pechiney Cadmium Removal and Uranium Recovery Processes
- IMI (Israel) used alcohols to purify acid but after HCL leaching
- Simplot developed a membrane process

2. Experimental

Normal lab equipment consisting of separating funnels, glass beakers, lab stirrer and other necessary accessories were used. Samples of KROPHOS-18 were supplied by KAMORPHOS, Mumbai, India & fertilizer phosphoric acid samples were taken from two local phosphate manufacturers, M/s. GSFC Ltd, Baroda and M/s. Sterlite Industries Ltd, Tuticorin. Standard commercially available industrial kerosene was used as a diluent.

The distribution coefficients were determined according to usual procedures. The concentrations of all the elements were determined by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The concentrations in the samples were determined by either the standard addition method or from a calibration line using pure ionic solutions of standard lab cos.

3. Procedure

Table I shows the raw phosphoric acid analysis. **Table II** shows the specification of the two pretreated Phos acid (PA) samples used for all the experiments. Standard industrial treatment processes were used to clean the acid of its anions and humus / organics as shown in Table II, before it entered the SX circuit for removal of cations. This is important since the huge amount of organics in green acid gradually clog the extraction capabilities of the reagent in the long run.

Table I – Analysis of Raw Fert Phosphoric acid (PA) (in grams per liter)

Constituent	Sterlite	GSFC
Gms/litre	54% P ₂ O ₅	29%P ₂ O ₅
H ₃ PO ₄ w/w	73-75%	38-40%
Uranium	0.0115	0.0090
Iron Fe	3.4	5.6
Calcium	4.2	2.7
Aluminium	3.3	3.7
Sulphate	29.7	22.3
Fluoride	0.42	17.7
Silica	<2	<6

Table II – Analysis of Pretreated Two grades of Phosphoric Acid (PA) (grams per liter)

Constituent	Sterlite	GSFC
Gms/litre	54% P ₂ O ₅	29%P ₂ O ₅
H ₃ PO ₄ w/w	73-75%	38-40%
Uranium	0.0115	0.0090
Iron Fe	3.4	5.6
Calcium	4.5	3.2
Aluminium	2.3	4.7
Sulphate	0.02	0.02
Fluoride	0.2	0.2
Silica	<1	<1

After pre-treating the acid for removal of anions (SO₄ & F) in the acid, the organics were removed by two different methods, namely,

- by adsorption on activated carbon (under redox conditions) AND
- by contact of acid with aliphatic diluents having high B.P's such as kerosene. This procedure was easier and could be run continuously with mixer settlers. After each run, this solvent was regenerated by water/dilute alkaline wash.

The acid was further reduced with lab scale Electrolytic Reduction apparatus to the required Redox potential to convert all U⁺ ions to tetravalent state & specifically reduce Iron to divalent (Fe⁺²) state to prevent it from entering the U⁺ stream. Ferro Phosphorus compound, Ferro-silicon compound, Iron filings, Zinc, Na₂S₂O₃ are some of the other available options for reducing the metals in acid.

In the initial experiments, the equilibrium time of extraction of metals between two phases was determined. Two (2) minutes of mixing time was found sufficient for equilibrium state, but in some tests, three (3) minutes was used.

4. Extraction behavior

The extractive selectivity of this Pyrophosphate KROPHOS-18 extractant follows certain general rules, which are correlated with the valency of the metal ions in the aqueous phase. Mono positive ions such as Na⁺, K⁺ etc., extract to an appreciable degree, while dipositive ions such as Ca⁺⁺, Mg⁺⁺ and Fe⁺⁺ and other similar ions extract to a better extent than the mono ions.

Tri positive ions of higher atomic weight such as Fe⁺³ and those of lanthanide and actinide series including cesium are extracted with high efficiency. However, lower atomic weight tri positive ions such as Al⁺³ are again extracted with medium effectiveness.

Tetra positive ions of heavy metal elements such as, thorium and uranium are extracted with the highest of distribution coefficients. Dipositive ions of the Uranyl type, UO₂⁺⁺, exhibit anomalous behavior such that very high extraction coefficients are obtained.

5. Results and discussion

Fig. 1 compares Extraction Co-efficient of metals from different H₃PO₄ concentrations with KROPHOS-18 and D2EHPA+TOPO extractant systems. The data clearly suggest KROPHOS-18 is a far stronger reagent than D2EHPA+TOPO system.

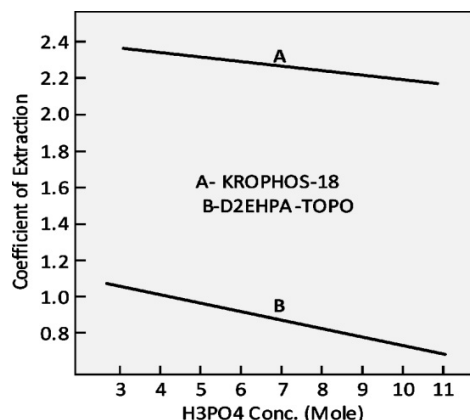


Fig 1- Plot for D^* for 0.2M KROPHOS-18 & 0.5M D2EHPA- 0.2M TOPO at different PA conc. Coefficient Extraction Vs H₃PO₄ (M) for Fe⁺ extraction

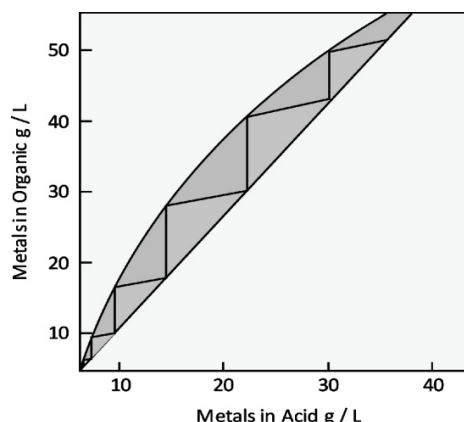


Fig 2 – McCabe Thiele diagram for metal Extraction from 29% P₂O₅ by 20% KROPHOS-18, In Organic Vs Conc. in green acid O:A – 3:1

The degree of saturation of organic phase was determined using various organic / aqueous phase ratios (O/A – 1/10 to 10/1) and 3 minutes contact time.

A 20% KROPHOS-18 (0.5M) solution in kerosene was found to show about 6- 7 stages of extraction necessary for optimum results of extraction and loading of extractant for all metals.

6. Effect of phase ratio on metals selectivity

Selectivity of metals with respect to U⁺ during extraction stage by the present extractant can be manipulated with change in O/A phase ratios and by altering the U⁺ to lower tetravalent state as shown in Table III.

Table III– Effect of Phase ratio (O/A), Single contact, on Metal extraction (%) using 20% KROPHOS-18 at 25°C, 29 % P₂O₅ acid, U⁺ extraction is under reduced conditions

Phase Ratios for Metal Recovery(O/A)	Metal Recovery	Phase Ratios for U+ Recovery O/A	Uranium Recovery
1/1	61.50%	1/10	71.40%
1.5/1	64.02%	1/7	78.35%
2/1	69.70%	1/5	88.70%
3/1	73.40%	1/3	92.22%
5/1	77.65%	1/1	96.76%

7. Stability tests of krophos-18 & stripping from loaded organic

The no. of recycles and stability of extractant are important parameters in solvent extraction systems. Table IV shows the metals recovery (%) versus number of solvent recycles for batch extraction tests.

Table IV – Stability Characteristics of 20% KROPHOS reagent, O/A-2/1 at 20°C, 54% P₂O₅ Phosphoric acid

Batch Cycle	Metals Recovery
1	93.80%
5	89.85%
9	87.70%
14	88.22%
20	87.68%
40	87.85%

Table V – Stripping Results for U⁺ with alkaline options at O/A=4:1 are summarized with 5% KROPHOS - ISODECANOL mixture

Nature of re-extractant	Molarity of re-extractant	Nature of Organic phase	
		Krophos – 18 5%	
		pH	Mg/l
(NH ₄) ₂ CO ₃	2M	8.4	43
(NH ₄) ₂ CO ₃	2M	8.5	21
NH ₄ OH	2M	8.5	29
NH ₄ OH + H ₂ O ₂	2M	8.8	<4

Experiments were conducted to investigate the stripping of metals and rare earths from solutions of KROPHOS-18 / Iso-decanol mixture in kerosene. Separate stripping chemicals were used for recovery of uranium & metals from referred cycles. Uranium was stripped in alkaline medium while the metals in acidic medium.

The redox conditions of the organic & aqueous streams play an important role both during extraction & stripping. 10% HF, 20% H₂SO₄, 8M HCL, 10M H₃PO₄ and alkaline carbonate solutions were used in these tests for checking various stripping related parameters. Table V & Table VI provide data on such investigations.

8. Effect of temperature on metal extraction

Temperature has a mild effect on the extraction of metals and uranium from the acid. Fig. 2 shows the results of such tests. Fig 3 indicates that D* values for KROPHOS-18 for all molar Phos acid extractions remains almost the same where as that for D2EHPA+TOPO decrease with rising temperature indicating greater stability of present novel extractant.

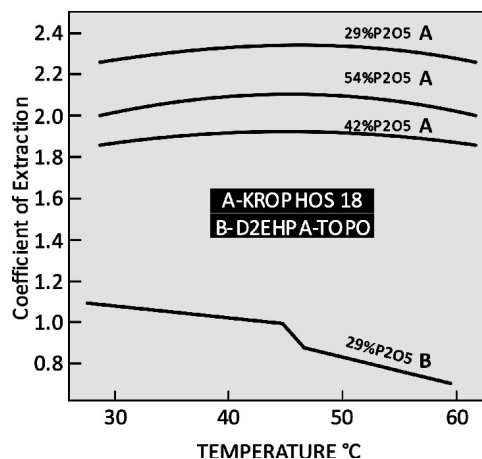


Fig 3 – Plot of KROPHOS -18 Extraction capability Coefficient Extraction Vs. Temp.

The following observations have been noted –

- Pretreatment for the removal of organics is a must, especially for the smooth running and continuous processing of the reagent with large amounts of fert phosphoric acid.

- b) The extraction kinetics of metals as well as uranium from phosphoric acid is fast by KROPHOS-18. In less than two minutes, equilibrium is attained.
- c) It is also seen that solvating agents such as TBP, Iso-decanol etc, are required for good solubility of KROPHOS-18 in diluents, proper phase separation and enhanced extraction.
- d) Fig 1 shows the extraction power of KROPHOS-18 i.e. the power a 0.2 M KROPHOS-18 solution is much higher than that of a 0.65 M D2EHPA – 0.2 M TOPO solution. This means that for a required process, much lesser KROPHOS-18 will be required than the pair of D2EHPA – TOPO synergistic mixture.
- e) Fig 3 shows that with the increase in temp up to about 55°C, the extraction behavior of the reagent is satisfactory. In practice too, the commercial grade filter acid is at 40-60°C. Table VI provides the data on stripping parameters of KROPHOS-18 reagent at various temperatures.
- f) Table III provides the data on extraction parameters of KROPHOS-18 reagent at various phase ratios. Although additional tests are needed for investigating reagent's extraction selectivity with different metal combinations in the aqueous phase.
- g) Fig 2 shows that 6 (six) theoretical extraction stages are required according to the McCabe-Thiele diagram, to reduce the concentrations of most of the cationic impurities from 29% P₂O₅ acid from about 35 gms/liter to about < 0.5 gms/liter (to ppm levels) by a (0.5M) 20% KROPHOS-18 solution in kerosene. The estimated results will agree with the laboratory data.

9. Conclusion

The current changes in the Phosphate & Uranium industry call well for a need to once again resume the practice of extracting uranium from fertilizer phosphoric acid. PHOSPURIN advantage of simultaneous purification of phosphoric acid is a double bonus.

The cost of extraction & sale of uranium simultaneous to phos acid purification compensates much of the cost of purifying the acid.

In other words, for a fertilizer plant recovering uranium, the resulting clean acid could be used for a number of downstream products, while much of the cost of producing such clean acid would be borne by uranium which is a good value product today.

From the point of view of general conservation also, it is far better to extract uranium from the rock than spread it over the fields that no one will ever be able to recover it again.

The SX process route is proven technology that can be used for the next generation of these plants. This current PHOSPURIN process is unique in its inherent style with no competition or comparison with any other past or current technologies available anywhere in the world.

Specific advantages being a dual benefit of purifying acid with uranium extraction, purification of any P₂O₅ acid, acid purification possible to both technical & food grade, higher +95% uranium recoveries, high purity uranium compared to other processes, simple equipment, considerable reduced new plant capital, lower utilities & operating costs etc, leading to a high return on investment for the PHOSPURIN extraction facilities.

The above results indicate that KROPHOS-18 can be commercially utilized for purification of green acid and recovery of precious rare earths like uranium from the acid. Lab bench scale mixer settler tests show that this is feasible, but additional pilot plant tests are necessary for the selection of optimum extraction system before venturing into commercialization of the process.

Table VI –Effect of Temp on stripping of Metals from 20% KROPHOS-18 / Kerosene with 10 M H₃PO₄, Conditions: O:A ratio=10:1, 8 stages, 2 minutes

Temps °C	Concentration of Metals		Metals Stripping %
	Organic Phase	Aqueous Phase	
10	0.41	0.59	61%
15	0.27	0.76	74%
20	0.13	0.87	85%
25	0.07	1.03	94%
30	0.05	1.04	97%
40	0.03	1.06	98%
50	0.01	1.04	99%
60	0.01	1.04	99%

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