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USE OF DIVERS' LIQUIDS IN THE REDUCTION OF HEAVY METALS DURING THE PRODUCTION OF PHOSPHORUS FERTILIZERS BY NITRIC ACID - AMMONIA PROCESS

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RESUME

Un nouveau procédé de séparation et d'épuration des engrais phosphatés et azotés des principaux macro-constituants communs / Ca, Ba, Mg, Sr, Na, K, Al, Fe / et d'un grand nombre d'oligo-éléments / Cd, Co, Ti, Th, U, terres rares, Zn, Cu, Mn, etc. / dans des systèmes non-aqueux.

Le premier stade du procédé technologique est la dissolution des phosphates dans l'acide nitrique :

$Ca_5(PO_4)_3 F + 10HNO_3$ -----> $5Ca(NO_3)_2 + 3H_3PO_4 + HF$

tous les autres éléments sont sous la forme de nitrates.

Le second stade est l'action de l'ammoniac sous pression de vapeur saturée et formation des divers liquides.

Le troisième stade consiste dans la séparation des phosphates d'ammonium insolubles dans les divers liquides de la phase liquide.

L'ammoniac est recyclé dans le système comme moyen de transport et réapprovisionné de temps en temps.

Toutes les réactions et les séparations sont effectuées dans un système non-aqueux plus facile et plus complet.

Les produits - engrais phosphatés nitreux - sont obtenus à l'état pur, sans métaux lourds. Il n'y a pas non plus de phosphogypse sous-produit en quantité.

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1. INTRODUCTION

The references on the applications of Divers' liquids in various chemical reactions (1-5) and chemical technology (6) are well documented.

This paper deals with the use of Divers' liquids in the production of phosphoric salts of ammonia, calcium, potassium and magnesium which can be used as NP, NPK and NPKMg fertilizers.

The process presented here was developed in order to cope with most of the impurities in phosphate rocks and also with the very troublesome by-product phosphogypsum.

The application of a non-aqueous system instead of the aqueous ones used to-date has many advantages.

2. PHYSICO-CHEMICAL BASIS OF THE PROCESS

The first step of the technological process is the reaction of phosphate rocks with nitric acid of different concentration:

$Ca_5(PO_4)_3F + 10\ HNO_3 \rightarrow 5\ Ca(NO_3)_2 + 3H_3PO_4 + HF$ (1)

$2\ Ca_5(PO_4)_3F + 14\ HNO_3 \rightarrow 3\ Ca(H_2PO_4)_2 + 7\ Ca(NO_3)_2 + 2\ HF$ (2)

$Ca_5(PO_4)_3F + 4\ HNO_3 \rightarrow 3\ Ca\ HPO_4 + 2\ Ca(NO_3)_2 + HF$ (3)

The optimum reaction temperatures are between 40 and 50°C.

After the reaction of the phosphate rocks with nitric acid ammonia under low pressure acts on pulp and Divers' liquid is formed.

The elements of IA, IIA, rare earth and other cations as nitrates form liquid phase under the action of gaseous ammonia under pressure 1000 hPa to 2000 hPa.

This ammonia system has completely different properties if we compare it with aqueous solution. These solutions named Divers' liquids containing the above cations as simple ions or ammoniates exert sufficiently high dissociation pressure, even at ambient temperature, that liberation of nitrates occurs after ammonia evaporation.

The cations having a charge greater than alkali metals, alkaline earth metals and rare earth metals exert stronger attraction forces with ammonia dipoles.

In spite of similarity between ammonia and water molecules, the chemical and physical processes are different in these media.

The dissociation constants, the rate of chemical reaction, solubility products, and so on, in liquid ammonia and in Divers' liquids differ greatly from those of water. In water solution ionic radius of Ca^{2+}, Cd^{2+} and the rare earth cations are roughly the same, whereas in liquid ammonia solution / e.g. in Divers' liquids / the complex ion $Cd\ NH_{3\ 6}^{\ 2+}$ is much larger and facilitates its separation.

3. PROCESS DESCRIPTION/GENERALITIES

The gaseous ammonia is introduced under low pressure into the pulp obtained during the action of nitric acid on phosphates and a solution is formed. Mixtures of phosphates as a solid phase containing $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_2Ca(HPO_4)_2$ and others are formed. This phase does not contain insoluble phosphogypsum. The separated solution - Divers' liquid - is a valuable source of different elements which one can separate with ion exchanger or during fractional precipitation in the course of ammonia evaporation. The evaporation of ammonia or separation on ion exchangers gives us different nitrates e.g. $Ca(NO_3)_2$, $[Zn(NH_3)_2]\ (NO_3)_2$, $[Cd(NH_3)_6]\ (NO_3)_2$, rare earths, nitrates, etc.

4. CONCLUSIONS

- A new process of separation and cleaning of phosphatic and nitrous fertilizers has been developed

- The separation of nitrates of IA, IIA, rare earths and a large number of rare elements: Cd, No, Ti, Th, U, Zn, Cu, Mn etc., is possible from the salts which can be used as NP, NPK or NPKMg fertilizers.

- The process consists of three main steps:
  - nitric acid action on phosphate
  - solution of phospho-nitrate pulp in gaseous ammonia under low pressure
  - separation process / fractional crystallization, or ion exchanger separation /

- The products, phosphatic - nitrous salts, are obtained in pure form without heavy metals or fluorine

- There is no troublesome by-product phosphogypsum in this new nitric acid-ammonia process.

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