Decreasing Iron Content in Phosphoric Acid Produced from New Valley Phosphates by Novel Precipitation Technique

Presented by

Hamdy Maamoun Abdel-Ghafar Hefny

A Thesis Submitted

To

Faculty of Science – Ain Shams University

For the Degree of

Ph.D

Chemistry Department

Faculty of Science

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(2019)

APPROVAL SHEET FOR SUBMISSION

Thesis Title: **Decreasing Iron Content in Phosphoric Acid Produced from New Valley Phosphates by Novel Precipitation Technique**

Name of candidate: **Hamdy Maamoun Abdel-Ghafar Hefny**

This thesis has been approved for submission by the supervisors:

1. Prof. Dr. Magdi Ahmed Mahmoud Ibrahim

Professor of Physical Chemistry - Chemistry Department, Faculty of Science, Ain Shams University

Signature:

2. Prof. Dr. Adel Mohamed Kamal Ismail

Professor of Hydrometallurgical Processing, Minerals Technology Department, Central Metallurgical Research and Development Institute (CMRDI), Cairo, Egypt

Signature:

3. Prof.Dr. Hassan El-Shall **(Passed away on December 2017)**

Adjunct Professor, Mineralogy Department, Faculty of Engineering, Cairo University & Full professor at Florida university, USA

Signature:

Prof. Dr. Ayman Ayoub Abdel-Shafi

Chairman of Chemistry Department

Faculty of Science, Ain Shams University

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PhD, Cairo University, 2016 - M.Sc., Cairo University, 2012 - B.Sc., Cairo University, 2008

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ABSTRACT

Student's Name: **Hamdy Maamoun Abdel-Ghafar Hefny**

Title of the thesis:

Decreasing Iron Content in Phosphoric Acid Produced from New Valley Phosphates by Novel Precipitation Technique

Degree: Ph.D (Inorganic Chemistry)

Abstract:

A method has been developed to decrease the iron content in phosphoric acid produced by the dihydrate wet process from open cast phosphate rock of Abu-Tartur mine in Egypt. In this method, oxalic acid was used to precipitate iron as ferrous oxalate dihydrate ($FeC_2O_4.2H_2O$). The achieved removal efficiency of iron was about 91% due to the low solubility of the precipitated salt in dilute phosphoric acid medium. The maximum P_2O_5 losses were less than 1.0 %. The optimum conditions of the oxalate precipitation method were obtained using synthetic dilute phosphoric acid (28 % P_2O_5) with iron content amounting 2.8 % Fe_2O_3. It was found that the clarification time, reaction temperature, P_2O_5 concentration and oxalic acid dose were 2 hours, 60 ^oC, 28% P_2O_5 and 7.5 g oxalic/100 g 28% P_2O_5 acid, respectively. These conditions were applied using wet-process phosphoric acid (28% P_2O_5) produced from the ore. Firstly, ferric ions in the acid were reduced to ferrous ions using iron scrap, followed by oxalic acid addition. Mostly all iron ions in the solution are in the divalent state at Electro Motive Force (EMF) values less than 275 mV. The solubility of ferrous oxalate dihydrate was measured at different temperatures and phosphoric acid concentrations. A study to recover oxalic acid from the precipitated $FeC_2O_4.2H_2O$ has been performed.

In addition, the fundamentals and basic studies of ferrous oxalate dihydrate ($FeC_2O_4.2H_2O$) crystallization including supersaturation, nucleation and crystal growth in simulated dihydrate phosphoric acid product with and without Cetyl Pyridinium Chloride (CPC) additive have been carried out. Oxalic acid and ferrous sulfate heptahydrate crystals were mixed with dilute phosphoric acid (28% P_2O_5) at 60 ^oC and the turbidity of the reaction mixture was measured at different time intervals. The induction time of ferrous oxalate dihydrate crystals was calculated at different supersaturation ratios ranging from 2.5 to 6.7. With increasing the supersaturation ratio, the induction time decreased. The nucleation rates are 46.4×10^{28} nuclei/cm^3.s and 50.2×10^{28} nuclei/cm^3.s at supersaturation ratio 6.7 with and without CPC addition, respectively. The surface energy increases with CPC addition compared to the baseline. In addition, the formed crystals are modified from cubic shape to rod-like shape with increasing CPC dose.

Also, the nucleation fundamentals and morphologies of iron II oxalate dihydrate crystals, $FeC_2O_4.2H_2O$, in deionized water and diluted phosphoric acid (28% P_2O_5) media were studied. Oxalic acid and iron II sulfate heptahydrate crystals were mixed with deionized water and diluted phosphoric acid (28% P_2O_5) media at 25 ºC with concentration range of 2.7 - 7.2 g/100 mL. The turbidity of the reaction mixture was measured at different time intervals and the induction time of iron II oxalate dihydrate crystals was calculated. It was found that, the increase of induction time in phosphoric acid medium is more than that in deionized water at the same concentration of iron II oxalate dihydrate crystals. The nucleation rates are 30.5×10^{28} nuclei/cm^3.s and 70.2×10^{28} nuclei/cm^3.s at 7.2 % concentration of iron II oxalate dihydrate in deionized water and phosphoric acid media, respectively. The surface energy increases in water medium compared to phosphoric acid medium. In addition, the formed crystals are converted from cubic to rectangular shape with increasing the concentration of iron II oxalate dihydrate in water medium. On the other hand, the crystals are converted from cubic to octahedral while changing the medium from water to phosphoric acid at 2.7 % iron II oxalate concentration.

Keywords: Oxalic acid; Phosphoric acid; Iron; Purification; Precipitation; Cetyl Pyridinium Chloride; Crystallization; Ferrous Oxalate Dihydrate; Nucleation.

Supervisors: **Signature**

1. **Prof. Dr. Magdi Ahmed Mahmoud Ibrahim**
2. **Adel Kamal Ismail**
3. **Prof. Dr. Hassan El-Shall**

Prof. Dr. Ayman Ayoub Abdel-Shafi

Chairman of Chemistry Department

Faculty of Science, Ain Shams University, Cairo, Egypt

Biography

- **B.Sc., 2008,** Chemistry Depart., Faculty of Science, Cairo Univ., Very Good.
- **Asfour for Mining & Refractories Co**., Qualified experience, 12/2008-2009.
- **M.Sc., 2012**, Chemistry Depart. (Inorganic), Faculty of Science, Cairo Univ.
- **El-Tebbin TPP**, CEPC, Qualified in industrial WT, 12/2009 - 8/2016.
- **12 Certificates** of Courses & Training (Chemistry, HR, Entrepreneurship).
- **Technical Support** with Arabia for Plastic Co. for Au, Ag & Cu Recovery (2010).
- **Ph.D., 2016**, Chemistry Depart. (Inorganic), Faculty of Science, Cairo Univ.
- A ward of Talented Young Researcher from **TYSP** at QIBEBT, CAS, China (April 2018 – March 2019).
- **ITEC**, Training Program on Fertilizer Quality Control, Central Fertilizer Quality Control & Training Institute "CFQCTI", Faridabad, India, 16/11/2017 - 20/12/2017.
- The **Best Presentation award** of Young Researcher, Mineral Engineering Conference MEC2016, 25-28 September 2016, Swieradow-Zdroj, Poland.
- **Honoring** of Egyptian Minister of Trade and Industry "Dr. Tarek Kabil" on my entrepreneurship project of eco-friendly and cost effective organic fertilizers, Nov. 2016.
- **9 Research Articles** have been published in prestige journals.
- **3 Oral Presentations** have been presented in international conferences (Egypt, Poland & Spain).
- Participating in research work of **4 International Projects**.

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I wish to express my deepest gratitude to all who helped me to accomplish this work, **my colleagues of Chemical and Electrometallurgy Laboratory at CMRDI** for their help and continuous cooperation.

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Hamdy Maamoun

Cairo, 2019

To anyone who pushes us to challenge

ourselves with or without meaning it,

Thank You