Kinetical Study of the Decomposition of Djebel ONK Phosphates by Nitric Acid

Allal Khoudia*

SERVITHEN – 8, rue Guillaume de Bois Nivard – F 78640 – Neauphle-le-Château.

Abstract

The development of industrial processes designed to produce efficient fertilizers is nowadays of great importance, particularly in the field of farming. One way of producing phosphate fertilizers is by reacting phosphate rocks with nitric acid. In the present work, the kinetics of this reaction has been studied using phosphate mineral from the Djebel Onk mine (Algeria) and measurements of the conversion of $\text{P}_2\text{O}_5$ have been carried out by gravimetry. The effects of various operating parameters, such as the reaction time, the reaction temperature, the nitric acid concentration and the size of the particle have been studied. The experimental conditions have been optimized and global kinetic data such as the reaction rate constant and the activation energy have been determined.

© 2012 The Authors. Published by Elsevier Ltd. Selection and/or peer-review under responsibility of the Scientific Committee of SYMPHOS 2011.

1. Introduction

Apatite rocks nowadays chemically broken down or decomposed at the manufacturing units of phosphate fertilizers with sulphuric acid according to the following reaction:

$$\text{Ca}_5(\text{PO}_4)_3\text{F} + 5 \text{H}_2\text{SO}_4 \rightarrow 5 \text{CaSO}_4 + 3 \text{H}_3\text{PO}_4 + \text{HF}$$

However, the use of this process has not been without negative consequences to the environment. Indeed, pollution problems threatening not only humans but also animals and plants have emerged. Hence, the development of practical and economical processes leading to the total or partial reduction of this pollution has been the subject of numerous studies, such as the reduction of phosphate ore with coke and silica in electric furnaces [1].

Despite the tremendous growth experienced by the development of techniques for treating industrial waste, and because of the presence of significant amounts of pollutants discharged, great difficulties in dealing with those pollutants generated by the fertilizer industry still persist. As an example, production of a ton of $\text{P}_2\text{O}_5$ causes the formation of about five tons of phosphogypsum which are discharged into the environment.

Hence, the recovery of this by-product, which is bulky and contains many pollutants, has been the subject of numerous studies [2]. It appears that phosphogypsum can be used in the production of building materials, as well as soil amendment.

Nevertheless, the substitution of sulphuric acid by nitric acid in the decomposition of phosphate ores can not only prevent the formation of this byproduct, but also reduce the consumption of $\text{H}_2\text{SO}_4$ and therefore reduce emissions of SOx.

* Corresponding author. Tel.: 33(0) 1 34 89 71 46; fax: 33(0) 1 34 89 08 78
E-mail address: kallal@servithen.fr
The nitric attack results in the formation of a solution of calcium nitrate and free phosphoric acid, based on the following reaction:

$$\text{Ca}_5(\text{PO}_4)_3\text{F} + 10 \text{ HNO}_3 \rightarrow 5 \text{ Ca(NO}_3)_2 + 3 \text{ H}_3\text{PO}_4 + \text{ HF}$$  \[2\]

This chemical decomposition leads to the production of fertilizers NP and NPK. It was found that this method can, in some cases, offers a number of advantages, such as:

- Reduction or elimination of sulphur consumption, which consequently leads to the reduction of sulphur oxides emissions in the flue gas
- Production of ready-to-use, composed fertilizers. In fact, these fertilizers are not coarsely, but intimately mixed at the molecular level.
- Use of natural gas as raw material for the production of ammonia necessary for the production of nitric acid

Moreover, it is possible to recover the energy released by this exothermic reaction (16.4 kcal / mole) during the process [3]. The advantage offered by such manufactured fertilizers is on one hand their high solubility [4] and on the other hand the possibility of converting them to nitrogen fertilizers such as ammonium nitrate, urea ammonium nitrate- or calcium ammonium nitrate [5].

2. Experimentation:

In the present work, the phosphate ore used was extracted from the mine of Djebel Onk (Algeria). Its mass composition is given in table 1. These concentrations were determined by X-Ray fluorescence and classic elementary analysis.

The kinetics of the chemical reaction was monitored by measuring the conversion rate of $\text{P}_2\text{O}_5$

<table>
<thead>
<tr>
<th>Substances</th>
<th>% mass</th>
<th>Substance</th>
<th>% mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>0,01</td>
<td>$\text{TiO}_2$</td>
<td>0,3</td>
</tr>
<tr>
<td>$\text{P}_2\text{O}_5$</td>
<td>28,8 – 29,5</td>
<td>$\text{Cd}$</td>
<td>11 ppm</td>
</tr>
<tr>
<td>$\text{SO}_3$</td>
<td>2,7 – 3,4</td>
<td>$\text{As}$</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>7 – 7,8</td>
<td>$\text{Hg}$</td>
<td>&lt; 5 ppm</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>2,2 – 2,4</td>
<td>$\text{MnO}$</td>
<td>14 ppm</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>0,35 – 0,4</td>
<td>$\text{Ni}$</td>
<td>20 ppm</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>0,4 – 0,5</td>
<td>$\text{Cu}$</td>
<td>20 ppm</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>49,5 – 50,0</td>
<td>$\text{Zn}$</td>
<td>85 ppm</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>1,4 – 1,7</td>
<td>$\text{Sb}$</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>$\text{Na}_2\text{O}$</td>
<td>0,3 – 0,36</td>
<td>$\text{Bi}$</td>
<td>&lt; 8 ppm</td>
</tr>
<tr>
<td>$\text{K}_2\text{O}$</td>
<td>0,1 – 0,2</td>
<td>$\text{U}$</td>
<td>&lt; 35 ppm</td>
</tr>
<tr>
<td>$\text{Cl}$</td>
<td>0,04</td>
<td>Organic</td>
<td>0,2 – 0,3</td>
</tr>
<tr>
<td>F</td>
<td>3,3 – 3,5</td>
<td>Compound</td>
<td></td>
</tr>
</tbody>
</table>

2.1. Operating procedure:

A given amount of phosphate ore is attacked by a nitric acid solution. The amount of acid used is 25% in excess of the stoechiometry. The operating parameters such as the temperature, the reaction time, the concentration of nitric acid, and the agitation speed are set in advance.

Nitric acid is first poured into a thermostatic container in which 15 grams of ore are added (this quantity was chosen so that the foam formed does not overflow). The mixture was stirred and, after a given time, removed from the thermostat, cooled down with a cryogenic system, and finally filtered under vacuum.
2.2. $P_2O_5$ measurement:

This measurement was carried out by means of the Perrin-Wilson-Daulgreen gravimetric method [6]. This method is based on the precipitation of phosphate ions with quinoleine phosphomolybdate in the presence of acetone. It is important to note that the $P_2O_5$ which is not an explicit kind of reaction “2” is in fact the anhydrous form of phosphoric acid. Indeed,

$$2 \text{H}_3\text{PO}_4 \rightarrow \text{P}_2\text{O}_5 + 3 \text{H}_2\text{O}$$  [3]

The method consists of adding 10 ml of HNO$_3$ and 20 ml of H$_2$SO$_4$ to the filtrate which is then made up to 1000 ml. The solution is left standing for half an hour (natural cooling), and filtered again before a volume of 5 ml is removed. The removed amount is poured into a vase to tare, in which 50 ml of distilled water, 15 ml of HNO$_3$ and 5 ml of a solution of quinoleine molybdate, are added. The mixture is then heated until the formation of a yellow precipitate. This is cooled down and then filtered in a sintered glass crucible with a porosity equal to 5 microns. The precipitate is first steamed for 45 minutes at 25 °C, then cooled in a desiccator and finally, weighed.

2.3. Determination of the conversion rate:

The conversion rate $\alpha$, expressed relatively to the $P_2O_5$, is given by the following relationship:

$$\alpha = \frac{m_{P_2O_5}}{(m_{P_2O_5})_0}$$  [4]

corresponding to the ratio of the $P_2O_5$ mass produced during the reaction under the form of phosphoric acid over the mass of $P_2O_5$ initially present in the ore.

The mass of $P_2O_5$ produced is given by:

$$m_{P_2O_5} = \frac{m_p \times f \times 1000}{5}$$  [5]

$m_p$ corresponds to the mass of the precipitate in grams and $f$ is an analysis factor depending on the stoechiometry of the reactions involved in the test.

3. Results and discussion:

![Graph showing variation of conversion rate versus time.](image)

Fig 1: Variation of conversion rate versus time.
Presented in figure 1, are the measurement results of the conversion rate versus time, at a temperature of 56 °C and a concentration of nitric acid equal to 59.8%. One can see that the reaction is relatively fast, particularly in the beginning, since 60% conversion is obtained after only 5 minutes of reaction and a maximum conversion rate, approximately equal to 95%, seems to be reached after only 60 minutes reaction.

The influence of the initial concentration of nitric acid \([\text{HNO}_3]_0\) on the conversion rate is shown in Figure 2. In fact, measurements of the conversion rate as a function of time for several acid concentrations between 30 and 59.8% were carried out at a temperature of 30 °C.

It can be shown that the increase in the concentration leads not only to an increase in the final conversion rate, but also in the speed of reaction represented by the slope of the curve defined by:

\[
\frac{d(m_{\text{P}_2\text{O}_5})}{dt} = m(\text{P}_2\text{O}_5)_0 \times \frac{d\alpha}{dt}
\]  

[6]

Where \(\frac{d\alpha}{dt}\) is the slope of the curve.
Since it has been shown in previous works \cite{7}, \cite{8}, \cite{9} that the partial order of the reaction with respect to HNO3 is equal to one, it seems therefore that this result is in perfect agreement with the kinetic laws, since the reaction speed is proportional to the concentration.

The results of measurements carried out at temperatures equal to 40, 50 and 60 °C, shown in Figures 3, 4 and 5, respectively, lead to similar conclusions as those in Figure 2.
The influence of the concentration of nitric acid on the final conversion rate is shown in Figure 6. A maximum rate is reached at a concentration approximately equal to 60%.

Since the reaction is the order of one in relation to the current concentration of HNO₃, hence:

$$\ln \frac{[\text{HNO}_3]}{[\text{HNO}_3]_0} = -k_t t$$

[7]
The use of equation 7, simultaneously with the results reported in Fig. 2, 3, 4 and 5, has led to the determination of the speed constant at 30, 40, 50 and 60 °C.

It is important to note that the nitric acid concentration was calculated at each moment, from the mass of P2O5 on the basis of reactions 2 and 3 and that each point, in Figure 7, represents the average value of the speed constant determined for each temperature, from Figures 2 to 5. The plot of the logarithm of this constant versus the inverse of the absolute temperature showed a good concordance with the Arrhenius law as shown in Figure 7.

The activation energy determined from the slope of the line (4.2 kcal / mol) appears to be in fairly good agreement with some values reported in the literature [10].

Figure 8 shows the results of the final conversion rate as a function of the reaction temperature at an initial acid concentration of 59.8%. One can see that this rate varies in the same direction as the temperature, reaching a maximum at 56 °C.

This increase can be explained kinetically through Arrhenius law, which says that the speed constant increases with the reaction temperature.
It was found however that beyond 56 °C, the conversion rate decreased. This decrease could be due either to a loss of nitric acid by evaporation causing the displacement of reaction 2 in the opposite direction to compensate for these losses (Laws of shifting balances) or to other kinetic factors such as the presence of parasitic reactions.

One of the parameters influencing the conversion is the specific area of mineral grains, hence, their diameter. Assuming that the particles are spherical and non-porous, it is possible to connect the specific area to the diameter through the following equation:

\[ S_m = \frac{6}{\rho \times d} \]  

[8]

Where \( \rho \) is the density of the particle in g/m\(^3\) and \( d \) is its average diameter in meters.

So an increase of the diameter leads to a decrease of the specific area, suggesting therefore a decrease of the conversion rate. To confirm this statement, measurements of the conversion rate as a function of grain sizes, varying between 50 and 500 microns were realized.

It can be seen, in fact, through Figure 9, that the final conversion rate is the highest between 50 and 150 microns and decreases beyond. A possible explanation is that there is a critical diameter of the particle over which the solution cannot reach the inner part of the mineral particle, resulting in a decrease of the final conversion rate.

Measurements realized by the BET method showed that a specific area of 16 m\(^2\)/g was obtained for a diameter of 80 microns, as compared to the value of 0.1 m\(^2\)/g, calculated from Equation 7. This result suggests that the ore particle is actually porous, and the chemical reactivity of phosphates is explained by the inner surface of the pores.
4. Conclusion

The results of this study showed that the phosphate ore of Djebel Onk can be fairly well decomposed by nitric acid. It has been observed throughout this study that the conversion rate of phosphate ore by nitric acid depends on the reaction temperature, concentration of reagents, reaction time, as well as other parameters, such as the contact surface in view of the heterogeneous nature of the reaction.

Conversion rates as high as 95% are obtained at a temperature of 56 °C, an acid concentration of 59.8 wt%, a particle size between 50 and 150 microns and reaction times of about 60 minutes.

Besides eliminating two major pollutants, sulphur oxides and phosphogypsum, the nitric attack offers other advantages over the sulphuric method, because the energy released during the reaction can be recovered and the calcium nitrate product offers the possibility to be converted to nitrogen fertilizer.

References